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STEREOCHEMISTRY OF THE DECOMPOSITION
OF AN OPTICALLY ACTIVE AZOALKANE

BY

THOMAS WALTER MOJELSKY



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled, STEREOCHEMISTRY OF THE DECOMPOSITION OF AN OPTICALLY ACTIVE AZO-ALKANE, submitted by Thomas Walter Mojelsky, in partial fulfillment of the requirements for the degree of Master of Science.

A C K N O W L E D G E M E N T S

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A B S T R A C T

Optically active 1-ethyl-1'-methyl-1-phenylazoethane was synthesized and decomposed at 100° and 125° in an inert solvent which was 1 M in butanethiol scavenger. At 100° the estimated retention of optical activity in the solvent cage of the unsymmetrical coupling product, 2,3-dimethyl-3-phenylpentane, was 41% and at 125° it was 17%. The percentage of optical retention in the decomposition of an optically active azoalkane may be used to determine the relative amounts of primary and secondary recombination. In the scavenged decomposition the isolated 2-phenylbutane had a small rotation which indicated retention of optical activity in the cage disproportionation reaction.

The absolute configuration of the coupling product and of 2-phenylbutane were correlated with the starting azo compound. There was overall net retention of configuration of the hydrocarbons produced in the cage.

An estimate of the cage effect in the decomposition of the azo compound was made. In benzene solvent, the lower limits were found to be 36% at 100° and 27% at 125°. These values are the mole percent of the unsymmetrical coupling product. The amount of disproportionation in the cage could not be determined because the olefins formed would react with the butyl thiyl radicals.

An enantiomorph of the unsymmetrical coupling product was synthesized and found to have an unexpectedly low rotation, $\alpha_D^{25} -0.4^\circ$ (1 1 dm., neat), 97% optically pure. Because of this low observed rotation, the rotations of the isolated coupling products were estimated from o.r.d. analysis. The calculated observed rotation of the "S" arrangement of the coupling product using Brewster's rules gave values of -9.5° and -2.2° , depending upon which value for the polarizability of the phenyl group was taken. The polarizability used to give the observed rotation of -9.5° has given more accurate estimates of optical rotation in other systems.

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I N T R O D U C T I O N

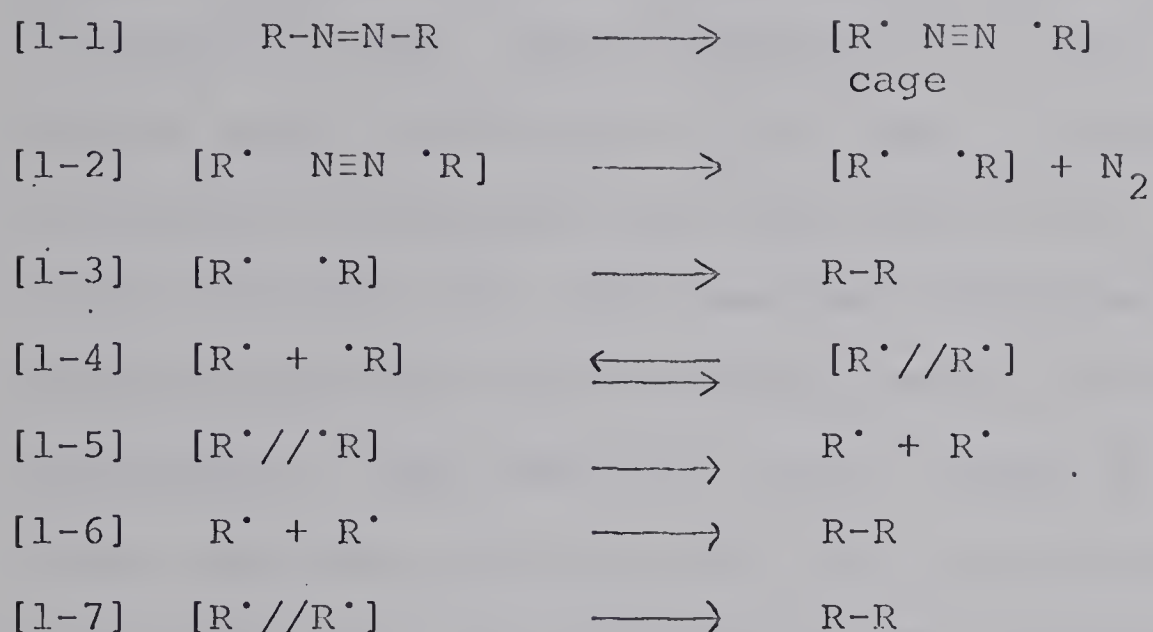
The objective of this investigation was to study the stereochemical integrity of free radicals formed in a solvent cage. Radicals were generated by the thermolysis of an optically active azoalkane.

The concept of a solvent cage was first formulated by Franck and Rabinowitsch (1) in 1934. It generally refers to the formation of a radical pair by the homolysis of a chemical bond. The two radicals thus formed in solution are subject to a unique and momentary relationship. Being formed simultaneously in the same location, the radical pair may couple together without diffusing away from each other. The probability of their mutual interaction is greatly increased. Such coupling is referred to as primary recombination.

According to Noyes (2) primary recombination in the cage takes place in a period that may be of the order of a vibration (10^{-13} seconds), and certainly less than the time between diffusive displacements (10^{-11} seconds). If coupling does not occur in this time interval, the radicals will diffuse out of their "solvent cage". During this random diffusion the fragments from a specific dissociation may re-encounter each other and undergo a secondary recombination. If secondary recombination does not take place within about 10^{-9} seconds (2) or one or two

diffusive displacements (3), the radicals will have diffused so far apart that the probability of re-encounter is negligible. Primary and secondary recombinations are collectively termed geminate recombinations.

Schematically this can be depicted in the following manner.



In equation [1-1] an azoalkane is used as the radical source. The squared brackets designate a solvent cage. Equation [1-3] depicts a primary recombination. Equation [1-4] depicts the diffusion of radicals out of the confines of the cage. Secondary recombinations are shown in equation [1-7]. Here the radicals have diffused only one or two molecular diameters. Equation [1-6] shows two radicals combining at random in the solution.

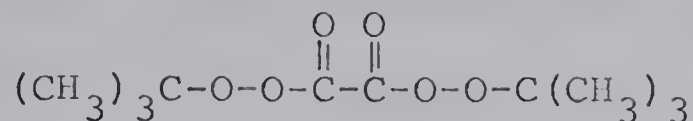
Cage reactions are those in which the original partners recombine to regenerate the parent molecule or

to generate some other derived molecule. One of the manifestations of a cage reaction is the decreased rate of formation of a specific compound compared to the rate in the absence of solvent. Lampe and Noyes (4) have studied the photolytic dissociation of iodine in solution. They interpreted the decreased quantum yield (compared to gas phase photolysis) as being due to iodine atoms recombining in the cage. Polymerization initiation by radicals has been shown to be less than 100% efficient (5). This has been explained as cage recombination of radicals which are not available for initiation. Some radicals can be trapped by scavengers. Those radicals which have not been trapped by efficient scavengers must have undergone cage recombination. This has been shown on the most commonly used azo polymerization initiator AIBN, azoisobutyronitrile (6).

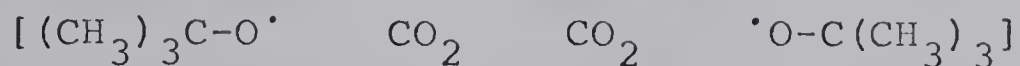
In principle products resulting from cage recombination may be observed in a number of systems which wholly or in part undergo homolytic cleavage in solution. The most frequently studied are the peresters, diacyl peroxides, and azo compounds. Radical coupling between C-O, C-N, and N-N is known to occur (7).

Bartlett and coworkers (8,9) have studied the thermolysis of peresters and have sought cage-produced products. They studied the decomposition of di-tert.-

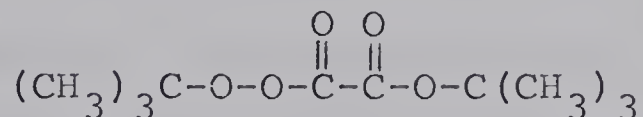
butyl-di-peroxyoxalate.



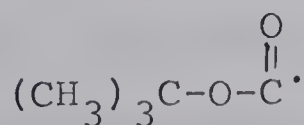
No di-tert.-butyl peroxide, the expected cage product, was detected. This was explained by the relatively large distance between the two tert.-butoxy radicals when they were first formed.



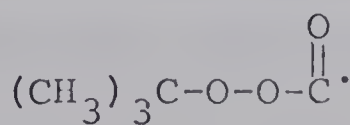
A true cage effect was observed when di-tert.-butyl monoperoxyoxalate was decomposed in the presence of galvinoxyl scavenger (10).



The product in this case was di-tert.-butyl carbonate, isolated in 35% yield. The carbo-tert.-butoxy radical, I, is able to survive the few collisions necessary for cage recombination. The carbo-tert.-butylperoxy radical, II, if formed, is so unstable that it decomposes in less time than is required to recombine with a tert.-butyl radical within the solvent cage.

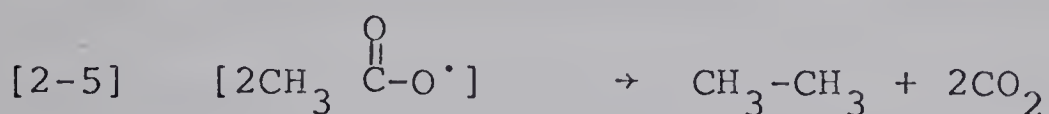
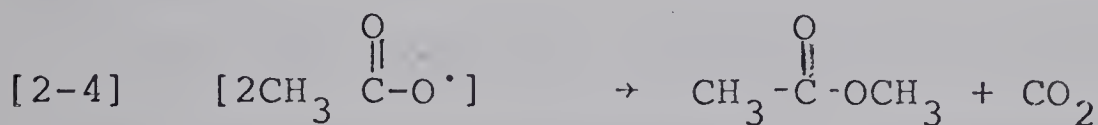
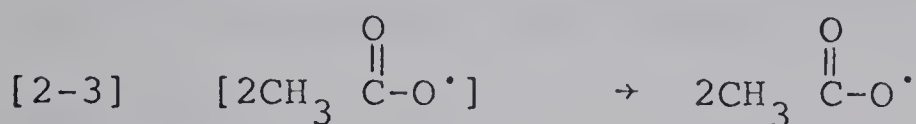
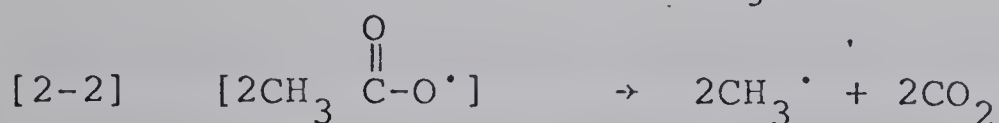
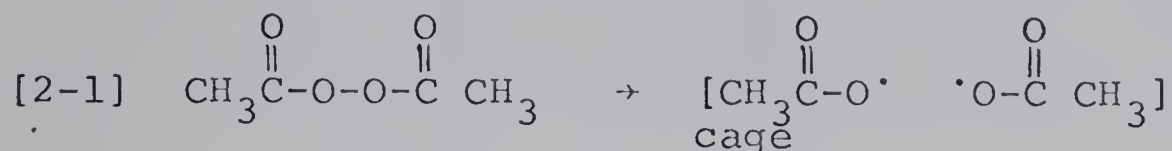


I



II

Diacetyl peroxide decomposition has been extensively studied (11-14). These investigators have studied the various products which are formed in the cage.

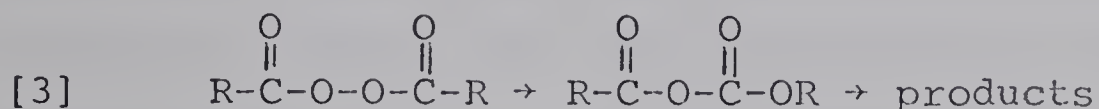


Szwarc and coworkers (12) attributed the formation of 19% methyl acetate, equation [2-4], in the presence of scavenger entirely to a cage reaction. No ester was isolated in the gas phase decomposition. Six percent of the methyl radicals, equation [2-5], dimerize in the cage.

Taylor and Martin (13) have studied diacetyl peroxide labelled with ^{18}O in the carbonyl oxygen. They observed at partial decomposition 38% scrambling of the ^{18}O label. This was ascribed to cage return of acetoxy radicals. Including the scrambling, over a 50% cage effect was observed.

Not all investigators accept a radical mechanism for the decomposition of other diacyl peroxides. Leffler (15)

has studied the decomposition of 4-methoxy-4'-nitro-benzoyl peroxide. He formulated a non-radical decomposition mechanism. In generalized form the mechanism is



This carboxy inversion reaction has been invoked by others (16,17) to explain the decomposition of other diacyl peroxides.

The most important reaction of aliphatic azo compounds is their decomposition to nitrogen and free radicals under the influence of heat or light. Of the many azo compounds synthesized, the most studied is azoisobutyronitrile (6,18). Hammond (6) has found a 20% yield of non-scavengeable radicals which form the dimer, tetramethylsuccinonitrile. More recently Bartlett (20,21) has reported the thermal and photolytic decomposition of azocumene. The cage effect was computed by kinetic means and found to be in the order of 25%. Hammond and Fox (22) have studied the thermolysis and photolysis of diethylazoisobutyrate. Identical decomposition processes and cage effects were noted.

Scavenging of radicals in the cage has been reported. Waits and Hammond (3) were able to scavenge completely 1-cyano-1-cyclohexyl radicals from the cage by using a high concentration of bromine as scavenger. They concluded that

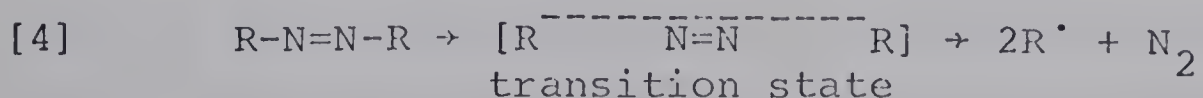
primary and secondary cage reactions could not be distinguished experimentally. Another report (23) concluded that in the decomposition of azoisobutyronitrile in the presence of iodine there was scavenging of secondary recombination of geminate radicals in photolysis. In thermolysis no geminate recombination took place.

The relationship between viscosity and cage effect has received considerable attention. Norman and Porter (24) reported "trapping" a free radical by cooling to 86°K. Bartlett (25) has reported the photolysis in solid solution at 77°K of meso and dl isomers of azo-bis-3-methyl-2-phenyl-2-butane. The resulting cage product coupling reaction was stereospecific, indicating complete retention of configuration in the cage. In liquids viscosity is inversely related to the temperature (26).

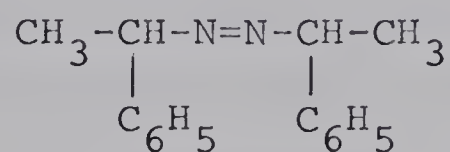
Lyon has studied the photochemical decomposition of azomethane in high density propane gas and observed a cage effect (27). Normally cage effects are absent in the non-condensed phase. Braun and coworkers (28) have noted a definite trend of decreasing rate constant with increasing solvent viscosity in the decomposition of diacetyl peroxide. The amount of cage products formed increased with increasing viscosity. Pryor and Smith (29) maintain that with increasing solvent viscosity,

the geminate pair of radicals separate more slowly and thereby result in larger proportions of internal return in the cage. No simple function of viscosity adequately relates the changes in cage effects with solvent (30). Pryor (29) has shown that the rate constant for disappearance of an initiator can be correlated with the viscosity of homologous solvents.

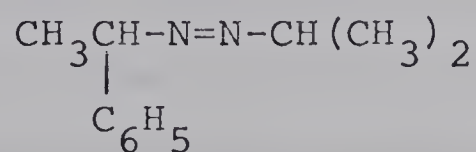
Azo compounds are characterized by the presence of an unsaturated nitrogen-nitrogen group ($-N=N-$). The aromatic azo compounds are highly coloured and commercially useful in the dye industry. The azo group is very stable (31). This is in sharp contrast to the aliphatic azo compounds which are relatively unstable and homolytically decompose under the influence of heat or light. The most important reaction of aliphatic azo compounds is their decomposition to nitrogen and organic free radicals. The driving force which accelerates this decomposition is the formation and expulsion of a very stable nitrogen molecule, dissociation energy 225 kcal/mole (32). Substituents capable of stabilizing the resulting free radicals will also lower the energy of activation for decomposition (32).



The mechanism of azo decompositions has been extensively studied. Seltzer (33) has studied the secondary alpha-deuterium isotope effect in the decomposition of 1,1'-diphenylazoethane.



The k_H/k_D ratio was found to be 1.27. This value is nearly twice the secondary alpha-deuterium isotope effect observed in reactions involving only one deuterium per reactive center. This observed ratio was taken as evidence that both C-N bonds break simultaneously in the transition state of the rate-controlling step. In the thermolysis of 1-methyl-1'-phenylazoethane (34)



and its deuterium-substituted analogs, the secondary alpha-isotope effect observed is interpreted as showing both C-N bonds stretching in the same step but to unequal degrees by the time the molecule reaches the transition state. Seltzer and Dunne (35) have proposed a two step reaction in the decomposition of 1-methyl-1-phenylazomethane. They believe that the methylazo radical, $\text{CH}_3-\text{N}=\text{N}^\cdot$, has

ephemeral existence. Kodama (36) has also suggested this radical's intermediacy in his study. Pryor's (29) internal return from the cage is in agreement with such a two step reaction.

The greater stretching of the benzylic carbon-nitrogen bond in the transition state of the decomposition of 2-methyl-2'-phenylazoethane (34) is due to the greater degree of resonance stabilization of the 1-phenylethyl radical. Differences in the rates of decomposition of azoalkanes are probably due to changes in the activation energies brought about by different degrees of resonance stabilization of the alkyl free radicals formed. Blackham and Eatough (37) have studied the activation energies for a series of isomeric azobutanes. They found the values to be a function of structure with the activation energy progressively decreasing on going from a primary to a tertiary group. Cohen and Wang (38) reported similar observations. Factors which contribute to stabilization of the radical products presumably contribute similarly to stabilization of the transition states and weakening of the C-N bonds. In a later study (39), Cohen and Wang found similar results in the various phenyl substituted phenylazomethanes. Overberger (40) found that this trend held in substituted azoalkanes and azonitriles.

In the literature there are reports of steric strain accelerating azo decompositions. Overberger and Berenbaum (41) found that branching on the alpha-carbon of substituted azo-bis-nitriles made little difference on the rate of decomposition. Branching on the beta-carbon increased the rate. Bicyclic azo compounds which have a greater angle strain decompose at an increased rate compared to less strained bicyclic azo analogs (42).

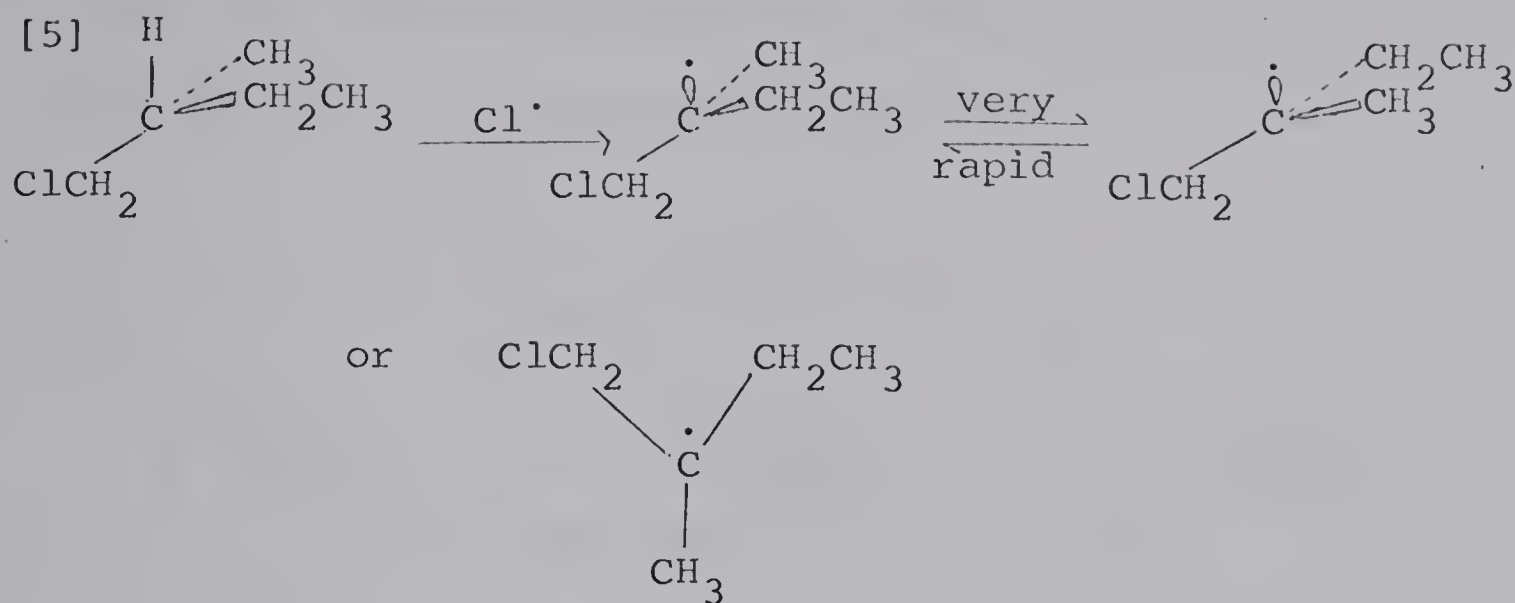
The configuration of a radical has yet to be unequivocally established, however, a planar geometry is favoured (43). The radical can be planar as in the carbonium ion geometry, tetrahedral, or a shallow pyramid. Electron paramagnetic resonance studies of methyl radicals (44) are interpreted to mean that the radical is planar, a deviation of 10 to 15 degrees from planarity, however, cannot be excluded. Bicyclic compounds cannot become planar at the bridgehead position. As a result bridgehead carbonium ions form very slowly (45). Bridgehead free radicals are formed much more easily (46).

Stereospecific addition of HBr in high concentration and at low temperatures (-80°C) to cis- and trans-2-bromo-2-butenes has been reported (47). Addition of excess HBr to the cis olefin resulted in meso dibromide; addition of HBr to the trans olefin gave the dl dibromide. The

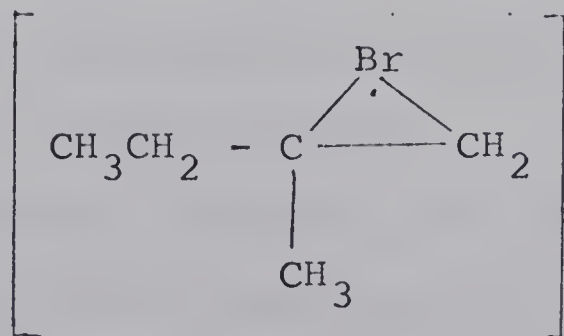
results indicate that intermediate asymmetric radicals have been trapped. At higher temperatures no stereospecificity existed. However, a bridged radical could also account for this selective reaction (48).

Kampmeier and Fantazier (49) concluded that cis and trans vinyl radicals generated from the thermal decomposition of tert.-butyl-cis- and trans-1,2-dimethylpercinamate equilibrate more rapidly than they abstract hydrogen from cumene. Greene and coworkers (50) studied the 4-tert.-butylcyclohexyl radical generated from dimethyl-(trans- and cis-4-tert.-butylcyclohexyl)-carbinyl hypochlorite. They concluded that the two generated radicals equilibrated to give a common non-planar intermediate 4-tert.-butyl-cyclohexyl radical.

The first attempt to generate an asymmetric tertiary free radical was done by Brown, Kharasch, and Chao (51). They performed a free radical chlorination on optically active 1-chloro-2-methylbutane. The desired product, 1,2-dichloro-2-methylbutane, was optically inactive. The racemic product could result either from a planar intermediate radical or from a rapidly inverting pyramidal radical.



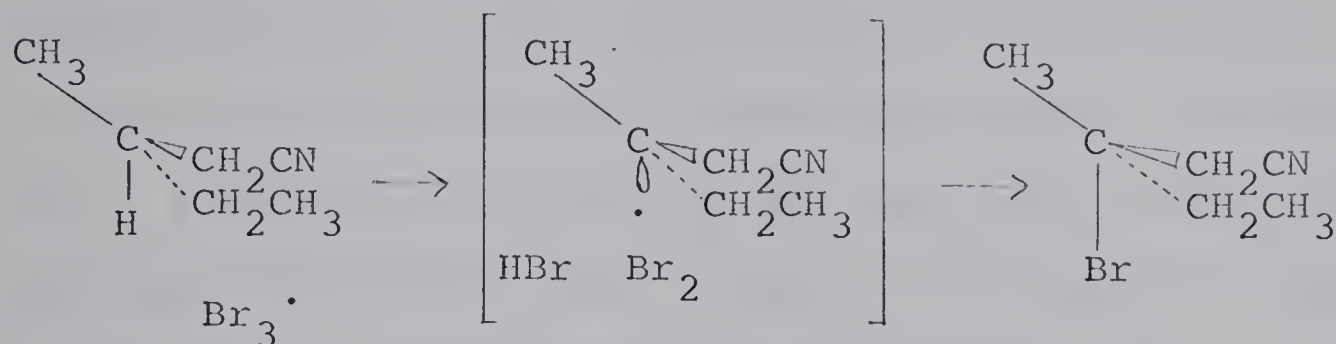
Skell and coworkers (48) performed photochemical bromination on optically active 1-bromo-2-methylbutane. The 1,2-dibromo-2-methylbutane product had optical activity. They concluded that bromine is a better transferring agent than is chlorine and that bromination is more selective than chlorination. Chlorination of the optically active bromohydrocarbon with tert.-butyl hypochlorite or Cl_2 yielded inactive 1-bromo-2-chloro-2-methylbutane. These results are taken as evidence for the formation of a bridged radical in the bromo compound



However Haig and Heiba (52) concluded that a pyramidal radical is formed as an intermediate in the photobromination of 3-methylpentanoic nitrile. Nitrile participation was

ruled out. If the hydrogen-abstracting species is Br_3^\cdot , then the following mechanism could hold:

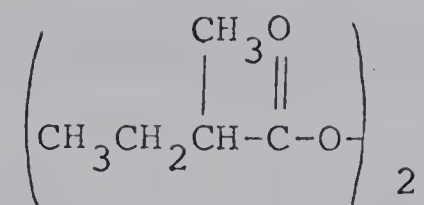
[6]



Bromine in the immediate proximity of the radical intermediate reacts before racemization can take place.

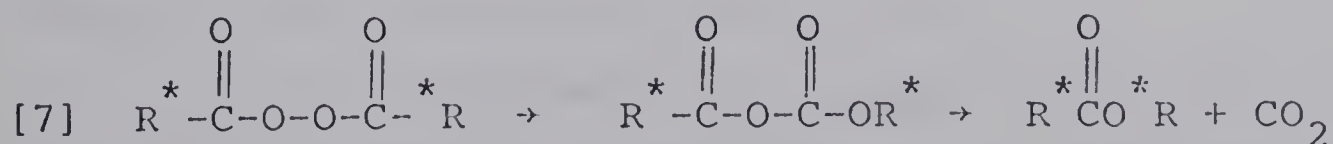
The decarbonmonooxylation of aldehydes is a free radical process (53). The vapour phase photolysis of optically active 2-methylbutanal has been studied by Gruver and Calvert (54). In the presence of iodine, the 2-iodobutane isolated was optically inactive. In the condensed phase the decarbonmonooxylation of optically active methylethylisobutylacetaldehyde resulted in optically inactive 2,4-dimethylbutane (55). It would appear that the intermediate radical is unable to sustain asymmetry in this reaction.

Kharasch and coworkers (56) have synthesized optically active di-(2-methylbutyryl) peroxide and studied its thermal decomposition in benzotrichloride. A product of the decomposition was optically active (2-butyl)-

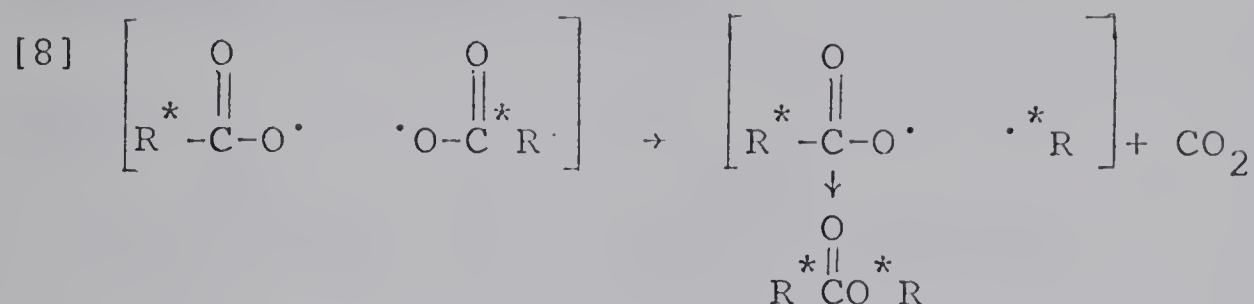


2-methylbutyrate. Upon saponification of this ester optical activity was seen in both the alcohol and the acid. A Walden inversion did not take place since both compounds were in the same series. In a similar study on di-(2-methyl-3-phenyl)-propyl peroxide in CCl_4 , DeTar and Weis (57) isolated an optically active ester. Upon saponification an optically active acid and about 25% racemized alcohol were recovered. Optically inactive 2-chloro-1-phenylpropane was also isolated.

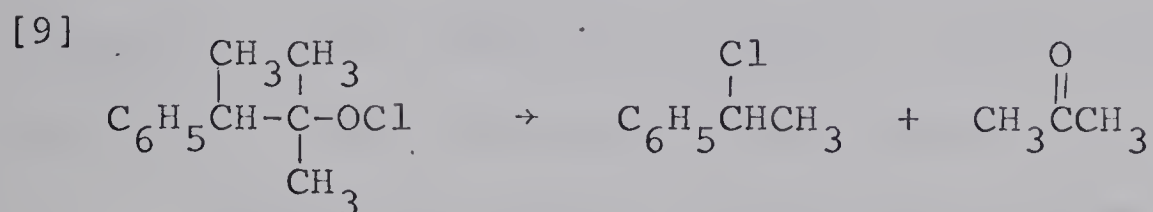
Attempts to isolate the optically active diacyl peroxide of hydratropic acid were unsuccessful (58). Only the products of the peroxide decomposition resulted. The optically active ester upon saponification gave an alcohol of 90% retention of configuration. D-Hydratropoyl chloride yielded D,D-2,3-diphenylbutane, corresponding to retention of configuration in the cage. Sources of optical activity of the alcohol in these examples could be from the carboxy rearrangement (15)



or a cage-trapped asymmetric radical.



The stereochemistry of the decomposition of 1,1-di-methyl-2-phenylpropyl hypochlorite has been investigated (59).

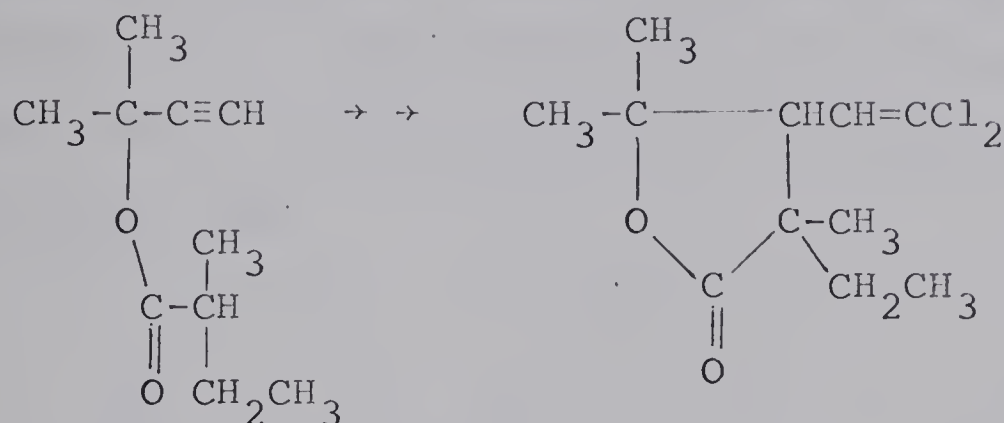


The beta-scission product, 1-chloro-1-phenylethane, was formed with about 2% optical activity and with retention of configuration. This could have arisen by an intramolecular decomposition or by a stereospecific recombination in the solvent cage. Studying the same system, Greene (60) reached a similar conclusion. The N-bromosuccinimide bromination of optically active 1-deutero-1-phenylethane gave a completely racemic 1-bromo-1-phenylethane or the deuterated compound (61).

A novel synthesis of a gamma-lactone with retention of optical activity has recently been published (62). An optically active propargyl ester is reacted with

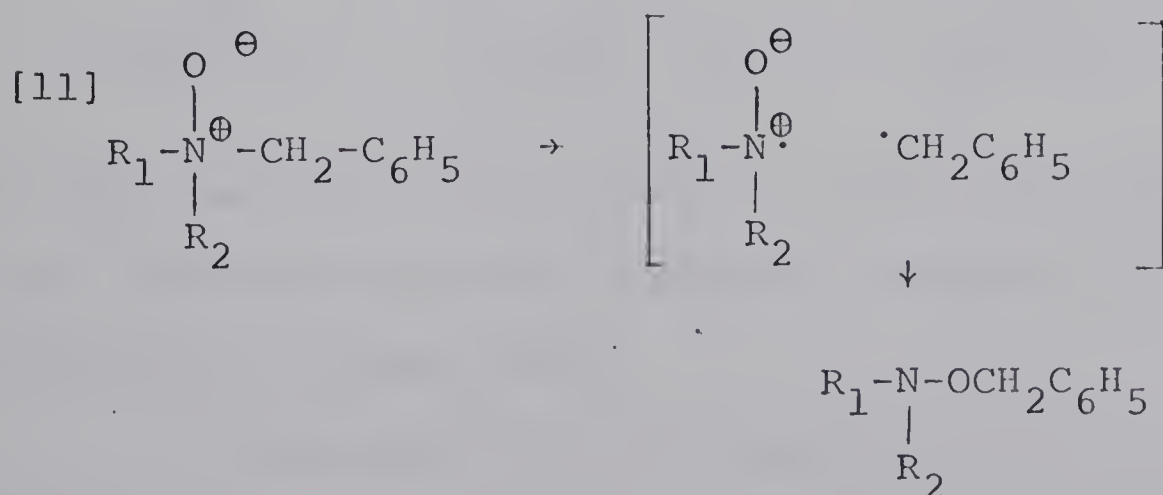
CCl_4 and benzoyl peroxide as initiator. The resulting lactone had optical activity.

[10]



Retention of optical activity is attributed to rapid trapping of the asymmetric radical before rotation about the bond to the carbonyl can take place.

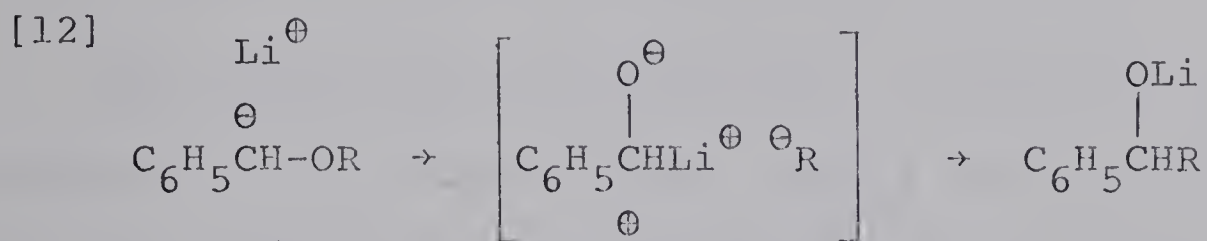
There are reports of optically active compounds undergoing rearrangements to give products with partial retention of activity. One such reaction is the Meisenheimer rearrangement of amine oxides to hydroxylamine derivatives (63).



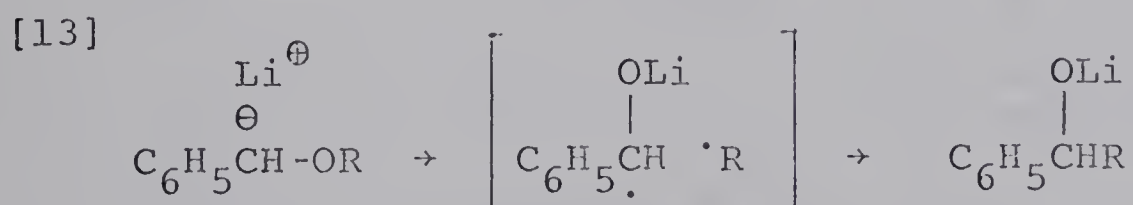
Radicals were observed by electron paramagnetic resonance. The hydroxylamine derivatives formed with

approximately 35% retention of optical activity.

A second reaction is the Wittig rearrangement of metalated benzylic ethers. The mechanism has been reported to be a cleavage-recombination reaction involving initial expulsion of the "migrating group" as a carbanion (65).



Secondary ethers rearrange with about 60% retention (65) and tertiary ethers with about 80% retention of configuration (66). Recently a free radical mechanism for this rearrangement has been postulated (64).

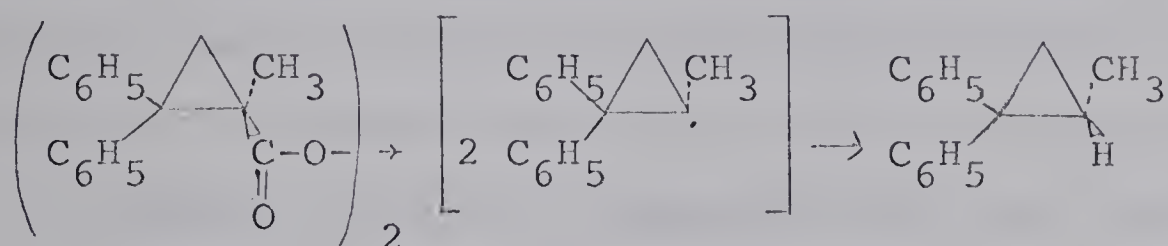


If free radicals are involved in these rearrangements, then these reactions are examples of retention of optical activity in solvent cages.

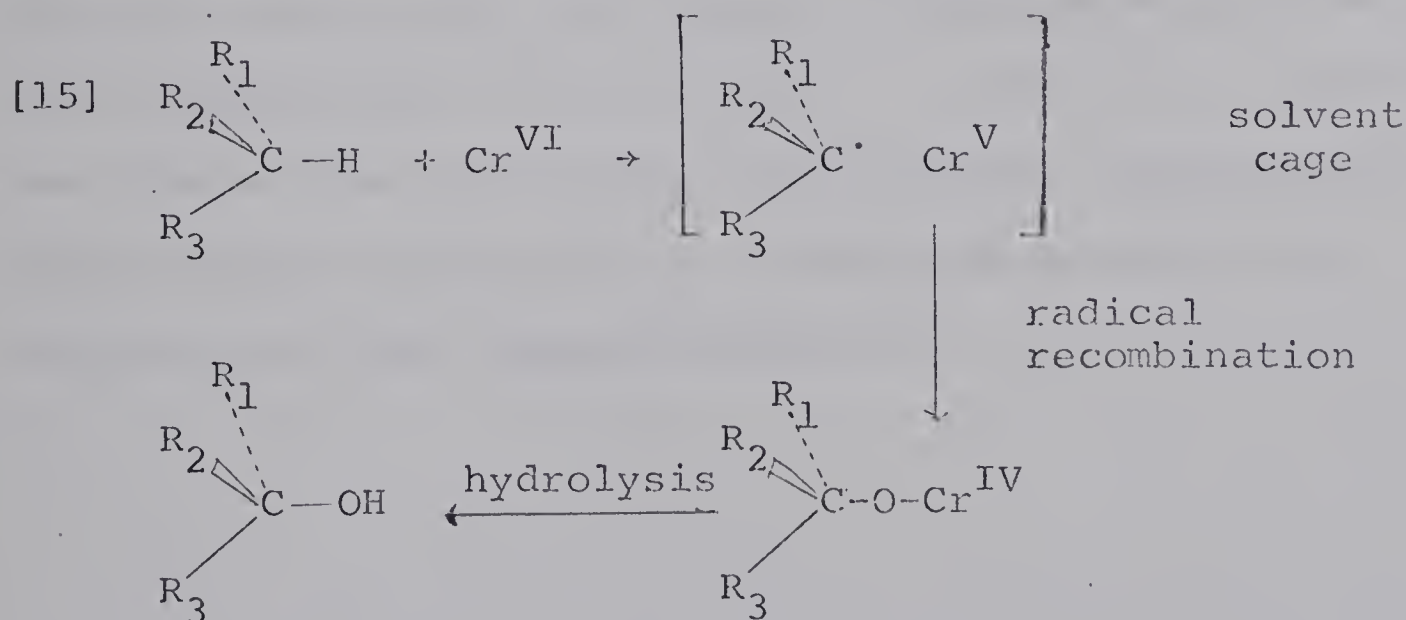
A disproportionation reaction occurring in the solvent cage has been reported by Walborsky (67). The optically active 1-methyl-2,2-diphenylcyclopropyl

radical abstracted a hydrogen atom in the cage to form the optically active hydrocarbon in 2% yield with about 34% overall retention of configuration.

[14]



The chromic acid oxidation of a hydrocarbon has been proposed to go through a free radical pathway (68). Wiberg (69) has studied the stereochemistry of the chromic acid oxidation of tertiary hydrocarbons. His proposed mechanism is



The radical in the cage retained its asymmetry. The chromium (IV) ester formed with retention of configuration. Hydrolysis formed the alcohol with 80 to 90% retention of

configuration. The partial racemization is explained by a not completely efficient cage recombination. A further example (69) of retention of configuration is the stereospecific oxidation of cis- and trans-decalins. Cis-decalin stereospecifically yields cis-9-decalol. Trans-9-decalol is formed from the oxidation of trans-decalin.

Several classes of compounds have been suggested to decompose by way of a free radical mechanism. As shown in some of the examples quoted, alternate decomposition mechanisms can also be proposed. Perhaps several different mechanistic decomposition pathways may be followed by a specific compound. Structural features, solvent properties, and reaction conditions may influence the decomposition route followed. In this work a system was chosen that would yield free radicals unambiguously upon thermal decomposition. Azoalkanes decompose exclusively by free radical formation.

R E S U L T S

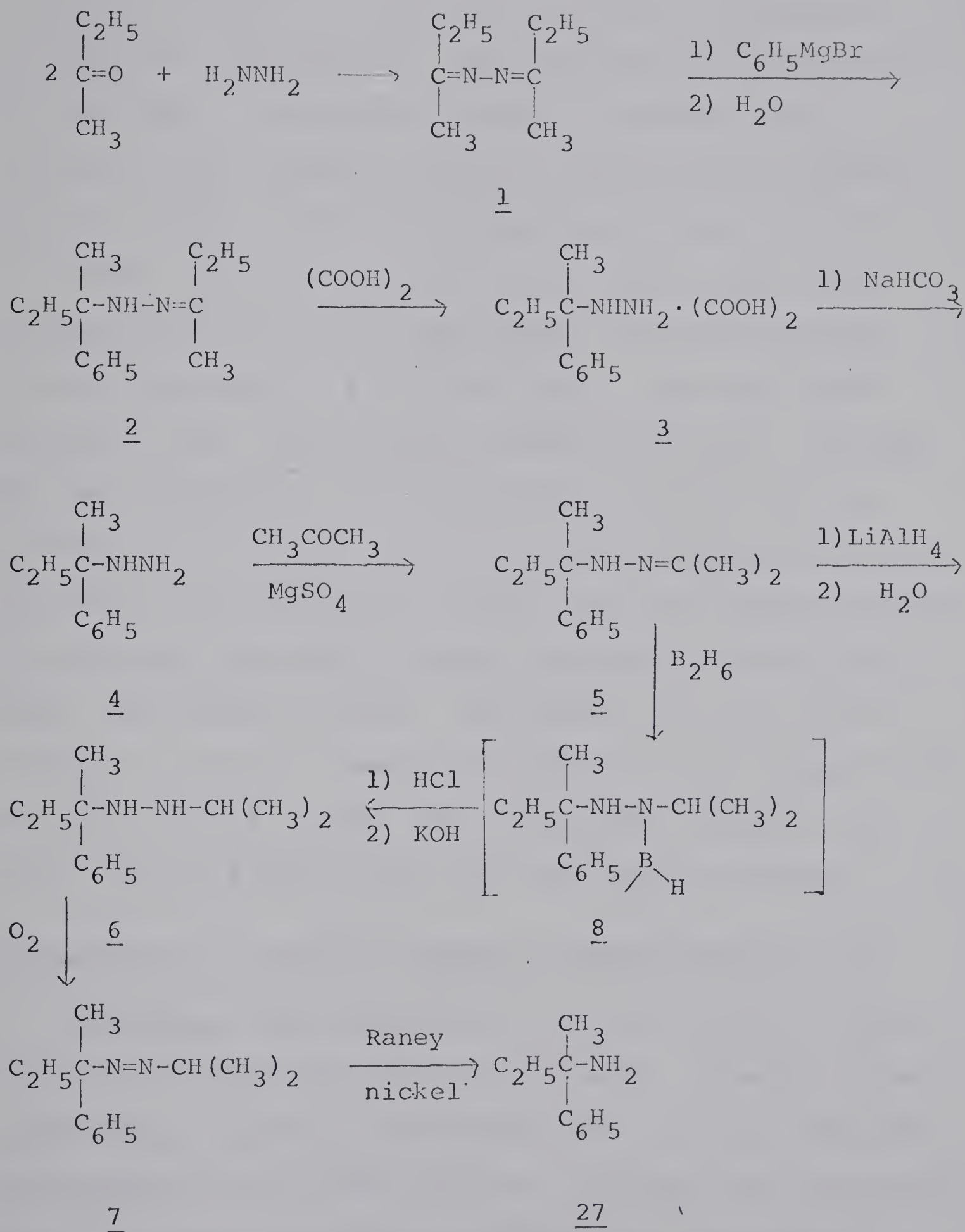
Preparation of acetone 2-phenyl-2-butylhydrazone, 5:

The compound 5 was prepared according to the general method of Overberger (90) for the synthesis of unsymmetrical azoalkanes. The procedure followed is outlined in Scheme 1. Condensation of 2 equivalents of methyl ethyl ketone with hydrazine is a facile reaction. The ketazine was isolated in 64% yield. There was no spectral evidence for the formation of methyl ethyl ketone hydrazone. Phenyl magnesium bromide addition to a C=N bond is not as rapid as it is to the C=O bond. For the formation of the intermediate hydrazone, methyl ethyl ketone 2-phenyl-2-butylhydrazone, 2, a reaction time of 5.5 days was found to be necessary.

After mild hydrolysis of the Grignard complex with saturated ammonium chloride, the intermediate hydrazone, 2, was hydrolyzed without isolation. A very suitable hydrolyzing agent is oxalic acid dihydrate which also forms an ether insoluble hydrazine oxalate salt. The salt may be stored or it may be decomposed to liberate 2-phenyl-2-butylhydrazine, 4. The entire extraction and isolation of 4 was done under a blanket of nitrogen to prevent air oxidation and carbonate formation.

The desired hydrazone, 5, was formed by condensing 2-phenyl-2-butylhydrazine and acetone in the presence of

Scheme 1



magnesium sulfate. It was not necessary to add acid to catalyze the condensation. The hydrazone, 5, was isolated in 84% yield. The nuclear magnetic resonance (n.m.r.) spectrum (CCl_4) showed a broad five proton phenyl absorption at $\tau 2.75$, a very broad singlet absorption at $\tau 5.5$, a two proton quartet centered at $\tau 8.15$ ($J=7.5$ cps), three singlets at $\tau 8.17$, $\tau 8.34$, and $\tau 8.65$, and a three proton triplet centered at $\tau 9.35$ ($J=7.5$ cps). The very broad singlet is due to the proton bonded directly to nitrogen. The two singlets at $\tau 8.17$ and $\tau 8.34$ accounting for six protons are the methyl protons of the isopropylidene group. Because of the restricted rotation about the carbon-nitrogen double bond, the methyl protons experience different magnetic and electric fields. The quartet at $\tau 8.15$ and the triplet at $\tau 9.35$ are associated with the ethyl group of the 2-phenyl-2-butyl moiety. The three proton singlet at $\tau 8.65$ is the signal of the tertiary methyl grouping.

Preparation of 1-ethyl-1'-methyl-1-phenylazoethane, 7:

Overberger (90) was able to reduce by catalytic hydrogenation the hydrazones that he prepared. Attempts to reduce acetone 2-phenyl-2-butylhydrazone, 5, using catalytic hydrogenation with three different catalysts were unsuccessful. Two chemical reduction methods were successfully applied to reduce 5 to the disubstituted hydrazine, 6,

which was consequently oxidized to the azo compound, 7.

Lithium aluminium hydride reduction of hydrazones has been reported (34). For the reduction of 5, the reaction time was prolonged to 72 hours from 19 hours as described. After hydrolysis and concentration, the residue showed a very complicated n.m.r. spectrum. It was a composite of unreacted hydrazone, hydrazine, 6, and the azo compound, 7. The hydrazine is easily oxidized in air. This discovery was exploited by oxidizing the di-substituted hydrazine in air. Stirring an unstoppered ether solution for eight hours was sufficient to complete the oxidation. Washing the ether with water removed the hydrogen peroxide formed. Air oxidation of hydrazines is more rapid and convenient than the mercuric oxide oxidation procedure of Overberger (90).

The separation of the azo compound from the starting not reduced hydrazone was accomplished by column chromatography on neutral alumina. The azo compound was a greenish-oil and its elution could be monitored visually. The non-polar 7 was eluted generally with the first two or three fractions of pentane. The hydrazone was adsorbed more strongly. Attempts to elute hydrazone in pure form from the column were not successful.

The structure of the azo compound was confirmed by spectroscopy. The compound had a weak ultraviolet absorption

at 368 mμ (ether), $\log \epsilon$ 1.46. In the infrared spectrum there was the characteristic isopropyl doublet at 1380 cm^{-1} and 1370 cm^{-1} as well as a weak absorption at 1580 cm^{-1} which could be the N=N stretching vibration (92). The n.m.r. spectrum (CCl_4) is also in accord with the azo structure proposed. The five proton phenyl absorption centered at $\tau 2.62$ belongs to the 2-phenyl-2-butyl grouping as do the three proton methyl singlet at $\tau 8.62$, the two proton quartet centered at $\tau 8.04$ ($J=7.5$ cps), and the three proton triplet centered at $\tau 9.34$ ($J=7.5$ cps). The methine multiplet of the isopropyl group is centered at $\tau 6.25$ ($J=6.5$ cps). Such a downfield chemical shift is expected of protons of a group bonded directly to the electron-withdrawing azo linkage. The six proton doublet of the isopropyl hydrogens is centered at $\tau 8.75$ ($J=6.5$ cps). Since all absorptions in the n.m.r. spectrum were accounted for, 7 was considered to be pure. No attempt to distil 7 was made. Distillation could result in partial decomposition of the azo compound. Compound 7 was purified by chromatography and concentration on the rotary evaporator until the n.m.r. spectrum was free of any extraneous peaks and the refractive index was constant.

Preparation of N-2-propyl-N'-2-phenyl-2-butylhydrazine, 6:

A second successful procedure for reduction of acetone 2-phenyl-2-butylhydrazone, 5, employed diborane. Diborane

has been used to reduce azobenzene and nitriles to hydrazobenzene and primary amines (70) respectively and oximes to N-alkylhydroxylamines (71). In a similar manner the carbon-nitrogen double bond of a hydrazone should also be reduced. It was found that reduction does occur but in variable yields (0-35%).

Diborane was generated in situ (93). An ether solution of the hydrazone, 5, was added to an ether solution of boron trifluoride etherate. Slow addition and rapid stirring could not prevent the formation of an oily, viscous material which probably was a complex formed between the hydrazone and boron trifluoride. To this solution was then added an ether solution of lithium aluminium hydride. The previously formed complex did not disappear at the end of the reaction and was probably the cause of the low and variable yield.

After addition of the lithium aluminium hydride a white solid formed. This material was to be hydrolyzed by the addition of aqueous acetic acid and then aqueous potassium hydroxide. After work-up and concentration, the residue had in the infrared spectrum (neat) a strong absorption at 2400 cm^{-1} which is the region of the boron-nitrogen stretching of simple addition compounds formed between borane and amines (72). It is then possible that structure 8 is an intermediate in this reaction. The most rapid and efficient cleavage of boron-nitrogen bonds results when anhydrous

hydrogen chloride is used (73). When bubbled into the solution a solid hydrochloride salt of the disubstituted hydrazine is precipitated. Decomposition of the salt and extraction under a nitrogen atmosphere yielded a reasonably pure sample of the hydrazine, 6.

In the n.m.r. spectrum (CCl_4) of 6 there was a five proton phenyl peak centered at $\tau 2.85$ of the 2-phenyl-2-butyl-group, a three proton singlet at $\tau 8.7$, a two proton quartet centered at $\tau 8.35$ ($J=7.5$ cps), and a three proton triplet centered at $\tau 9.4$ ($J=7.5$ cps). There was a doublet of doublets centered at $\tau 9.1$ ($J=6$ cps) for the six protons of the methyls of the isopropyl group. The two proton singlet at $\tau 7.32$ was exchanged by deuterium oxide and belonged to the protons attached to nitrogen. The methine proton multiplet was centered at $\tau 7.32$ ($J=6$ cps). The chemical shift of this multiplet was approximately 1 unit upfield from that of the azo compound, 7. In the spectrum there were present small peaks ascribable to the azo compound.

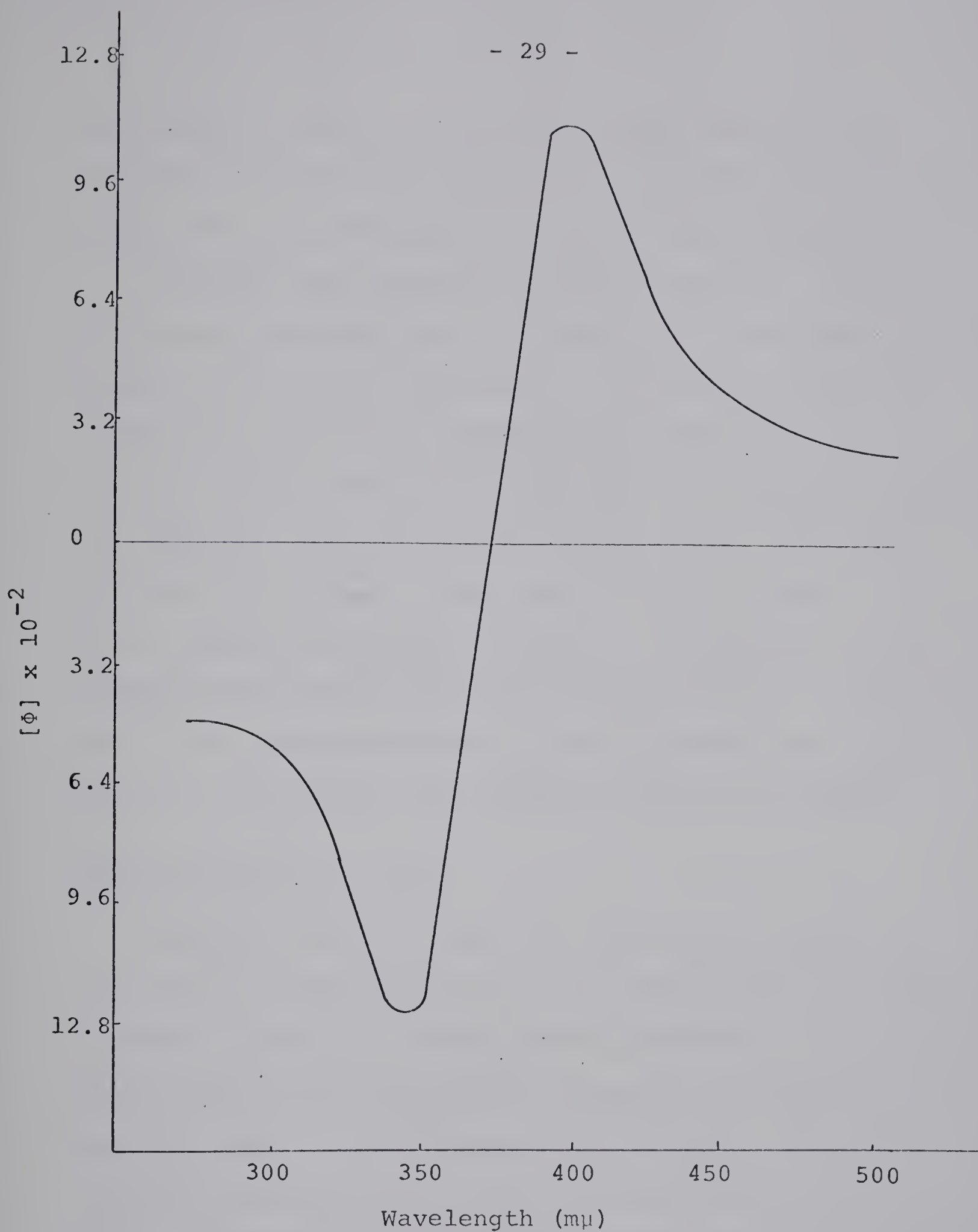
Resolution of N-2-propyl-N'-2-phenyl-2-butylhydrazine, 6:

Since the disubstituted hydrazine was very susceptible to air oxidation and since this hydrazine was required for resolution, a rapid method for hydrazine salt formation was needed. It was found that salt formation between hydrazine

and dibenzoyl tartaric acid could take place in ether solution. This was conveniently accomplished by filtering the ether solution after work-up of the lithium aluminium hydride reduction directly into an ether solution of (-)-dibenzoyl tartaric acid. A precipitate formed immediately. The filtrate was set in the refrigerator for two days and more precipitate formed. The precipitated salts were twice recrystallized from a 2 : 1 solvent mixture of ethanol and water. The salt was decomposed and the hydrazine, 6, was oxidized. The reaction mixture was chromatographed on neutral alumina. After concentration the n.m.r. spectrum of the azo compound obtained was free of extraneous peaks. If the hydrazine dibenzoyl tartrate salt were recrystallized a third time, the optical activity of the azo compound obtained upon oxidation of the liberated hydrazine did not change from $\alpha_D^{25} +35.5^\circ$ (1 1 dm., neat). The optical rotatory dispersion (o.r.d.) curve of (+)-7 (25 mg in 10 ml cyclohexane) is shown in Figure 1 and has typical positive Cotton effect curve characteristics (74).

Attempted isomerization of 7:

To determine the optical purity of (+)-7 obtained after resolution of the hydrazine, 6, several approaches were attempted. The first approach was to isomerize 7 to the hydrazone, 5, and then hydrolyze 5 to the monosubstituted



Cyclohexane 25mg/10ml

Figure 1. Optical rotatory dispersion curve of (+)-7.

hydrazine, 4, which has been previously resolved (91).

Anhydrous hydrogen chloride in an ice-cooled ether solution of the azo compound, 7, did not effect the isomerization.

Potassium tert.-butoxide (1 equivalent) in a solution of dimethyl sulfoxide and 7 (1 equivalent) did bring about isomerization to the hydrazone. A reaction time at room temperature of 4 hours resulted in an estimated 50 : 50 mixture (n.m.r. spectrum analysis) of the hydrazone and the azo compound. Prolonging the reaction time to 12 hours decreased the amount of azo compound in the mixture. The n.m.r. spectrum, however, indicated the presence of other unidentified products in addition to hydrazone, 5. Hydrolysis of the reaction mixture to the monosubstituted hydrazine, 6, with oxalic acid dihydrate was not successful.

Hydrogenolysis of (+)-7:

A second attempt to determine the optical purity of (+)-7 was to hydrogenolyze the azo compound and to isolate 2-phenyl-2-butylamine whose maximum rotation is known (114). Raney nickel hydrogenolysis of aromatic azo compounds and dyes has been successfully carried out (76). With these compounds hydrogenolysis takes place generally after one hour. Extension of such reaction conditions to an aliphatic azo compound, (+)-7, was not completely effective. Only one equivalent of hydrogen was consumed. However, if the hydrogenated solution were held at reflux for 11 hours over Raney

nickel, hydrogenolysis products could be isolated. Not all of the azo compound was hydrogenolyzed under these conditions. Pyrolysis product peaks were seen on the gas chromatogram when the hydrogenolysis reaction solution was injected in the gas chromatograph. These were due to the azo compound which decomposed on the gas chromatograph column.

(-)-2-Phenyl-2-butylamine, $\alpha_D^{25} -14.0^\circ$ (1 l dm., neat), was isolated from the effluent of the gas chromatograph. Kosower (114) has reported $\alpha_D^{25} +16.8^\circ$ (1 l dm., neat) for the amine resolved as the maleate salt. Cram (91) has reported $\alpha_{546}^{25} +18.2^\circ$ (1 l dm., neat). Assuming that Kosower's amine was completely resolved, the azo compound, (+)-7, $\alpha_D^{25} +35.5^\circ$ (1 l dm., neat), was 84% resolved after two recrystallizations of the hydrazine-dibenzoyl tartrate salt.

Preparation of 2-phenyl-2-butylamine, 27:

This amine was prepared in order to have an authentic 27 to compare with that amine obtained from hydrogenolysis of (+)-7. Hydratropic acid can be converted to 1-phenylethylamine with retention of configuration by the Schmidt reaction procedure (108). (-)-2-Methyl-2-phenylbutanoic acid (-)-11, $[\alpha]_D^{25} -29.06^\circ$ (c 4.8, benzene), was reacted analogously with sulfuric acid and sodium azide. The isolated primary amine (infrared absorption (CCl_4) at 3500 cm^{-1} and 3400 cm^{-1}) was aniline. The n.m.r. spectrum (CCl_4) showed a broad five proton absorption in the region between $\tau 2.8$ and $\tau 3.7$ and a

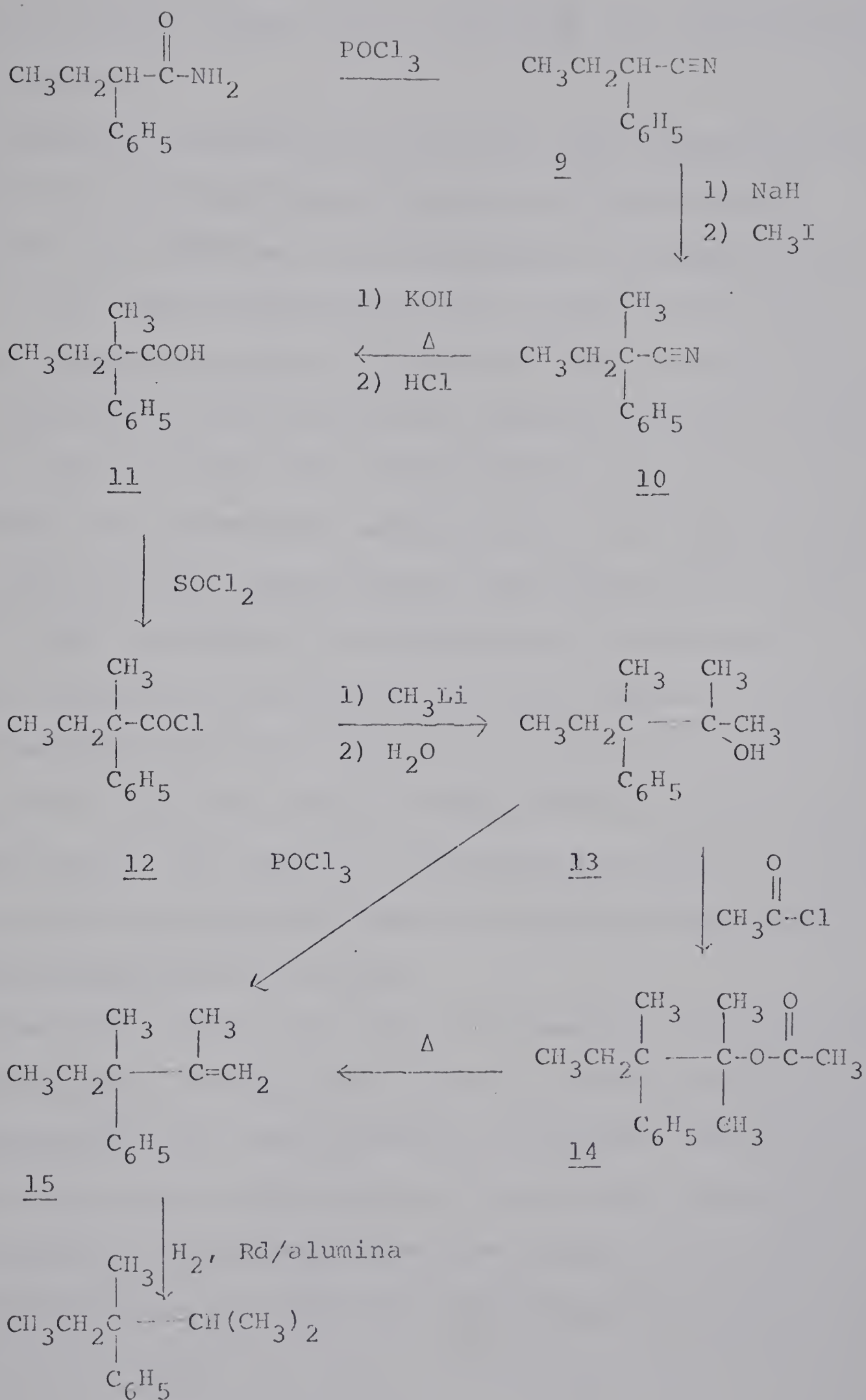
broad two proton singlet at τ 3.7.

The Curtius rearrangement of 2-methyl-2-phenylbutyryl azide to 2-phenyl-2-butylamine with complete retention of configuration has been previously described (91). Twenty-two percent optically pure (+)-2-methyl-2-phenylbutanoic acid, $[\alpha]_D^{25} +6.60^\circ$ (c 4.8, benzene), was converted to (-)-2-phenyl-2-butylamine, $\alpha_D^{25} -3.42^\circ$ (1 1 dm., neat). Based on these figures, optically pure 27 would have $\alpha_D^{25} -15.7^\circ$ (1 1 dm., neat). Cram (91) has reported $\alpha_{546}^{25} +18.2^\circ$ (1 1 dm., neat). Kosower (114) has reported $\alpha_D^{25} +16.8^\circ$ (1 1 dm., neat). The n.m.r. spectrum (CCl_4) of (-)-27 showed a two proton singlet at τ 8.74 which was eliminated upon shaking with deuterium oxide.

Preparation of 2,3-dimethyl-3-phenylpentane, 16:

The synthesis of the unsymmetrical coupling product, 2,3-dimethyl-3-phenylpentane, 16, expected from the decomposition of 7 is shown in Scheme 2. The sequence of reactions was chosen to insure that once the asymmetric center was formed, further reactions on the compound were of a sufficiently mild nature to prevent racemization. 2-Methyl-2-phenylbutanoic acid, 11, was obtained from a sequence of steps similar to those previously described (95). Compound 11 was resolved as the quinine salt (98). After 4 recrystallizations of the salt and subsequent acidification, white prismatic crystals of 11, m.p.

Scheme 2



87-87.5°, $[\alpha]_D^{25}$ -29.06° (c 4.8, benzene) (97% optically pure) were obtained.

2-Methyl-2-phenylbutyryl chloride, 12, prepared in 93% yield from 2-methyl-2-phenylbutanoic acid and thionyl chloride, was added to a two-fold excess of methyllithium (99). The infrared spectrum (CCl_4) of the crude product showed alcohol absorption at 3560 cm^{-1} and carbonyl absorption was due to the formation of 3-methyl-3-phenyl-2-pentanone. After allowing the alcohol-ketone mixture to react a second time with excess methyllithium, the infrared spectrum (CCl_4) of the product showed absorption only at 3560 cm^{-1} . This procedure for synthesizing 2,3-dimethyl-3-phenyl-2-pentanol from the acid chloride appears to be more advantageous than that reported by Cram and co-workers (75). They used a ten-fold excess of methyllithium and the appropriate ester. The reaction was repeated three times before the alcohol was separated from the ketone by chromatography of the alcohol-ketone mixture.

The crude alcohol, 13, was acetylated by acetyl chloride in N,N-dimethylaniline (100). The 2-acetoxy-2,3-dimethyl-3-phenylpentane, 14, was obtained in 58% yield. The olefin, 15, was obtained by pyrolysis of a methanolic solution of the acetate. The infrared spectrum (CCl_4) of the olefin showed absorptions at 1635 cm^{-1} and 895 cm^{-1} (terminal olefin).

The n.m.r. spectrum (CCl_4) showed a five proton phenyl absorption singlet at $\tau 2.8$, a two proton olefin singlet at $\tau 5.05$, a two proton quartet ($J=7$ cps) centered at $\tau 8.14$, a three proton methyl triplet ($J=7$ cps) centered at $\tau 9.23$, and two methyl singlets (6 protons) at $\tau 8.52$ and $\tau 8.66$.

An alternate route to 15 is via dehydration of 2,3-dimethyl-3-phenyl-2-pentanol, 13. The alcohol and phosphorus oxychloride in pyridine were heated to gentle reflux for several hours. The crude product obtained after work-up was chromatographed on neutral alumina. The n.m.r. and infrared spectra were identical with those obtained from acetate pyrolysis.

(+)-2,3-Dimethyl-3-phenyl-1-pentene, (+)-15, was synthesized in exactly the same manner as was 15. The starting compound was 97% optically pure (-)-2-phenylbutanoic acid, $[\alpha]_D^{25} -29.06^\circ$ (c, 4.8, benzene). The acetate pyrolysis method was used to yield (+)-15 which had $\alpha_D^{25} +11.3^\circ$ (1 l dm., neat).

The saturated hydrocarbon, 16, was formed by catalytically hydrogenating the olefin, 15, over 5% rhodium on alumina. The theoretical amount of hydrogen was taken up in the first hour, the hydrogenation was, however, allowed to proceed for 24 hours. Analysis by g.l.c. showed that 16 was at least 97% pure. No starting olefin was detected. The retention times of the two hydrocarbons were different.

Also no terminal olefin absorption at 1635 cm^{-1} and 895 cm^{-1} was seen in the infrared spectrum (CCl_4).

In the n.m.r. spectrum of 16 (CCl_4) there was a five proton phenyl singlet at $\tau 2.86$, a complex multiplet between $\tau 7.9$ and $\tau 8.7$, a three proton methyl singlet at $\tau 8.83$, a three proton methyl triplet at $\tau 9.1$ ($J=7\text{ cps}$), and two sets of doublets accounting for 6 protons centered at $\tau 9.1$ and $\tau 9.35$ ($J=6.5\text{ cps}$). The two isopropyl methyls adjacent to an asymmetric center must experience different electric and magnetic environments and this results in the appearance of doublets at different chemical shift.

(+)-2,3-Dimethyl-3-phenyl-1-pentene, $\alpha_D^{25} +11.3^\circ$ (1 1 dm., neat) was hydrogenated over 5% rhodium on alumina. The same precautions were taken as previously. Analysis by g.l.c. indicated greater than 98% purity and showed the absence of olefin, (+)-15. The saturated hydrocarbon, (-)-16, had a disconcertingly low rotation, $\alpha_D^{25} -0.4^\circ$ (1 1 dm., neat). The o.r.d. curve, 10.5 mg per ml methanol, is shown in Figure 2. The lowest utilizable wavelength is 280 m μ . If a lower wavelength is used, the photo-multiplier voltage rapidly increases to maximum value and negates any meaningful reading. Lower concentrations of (-)-16 did not give a satisfactory dispersion curve, instrumental sensitivity did not permit the use of higher concentrations.

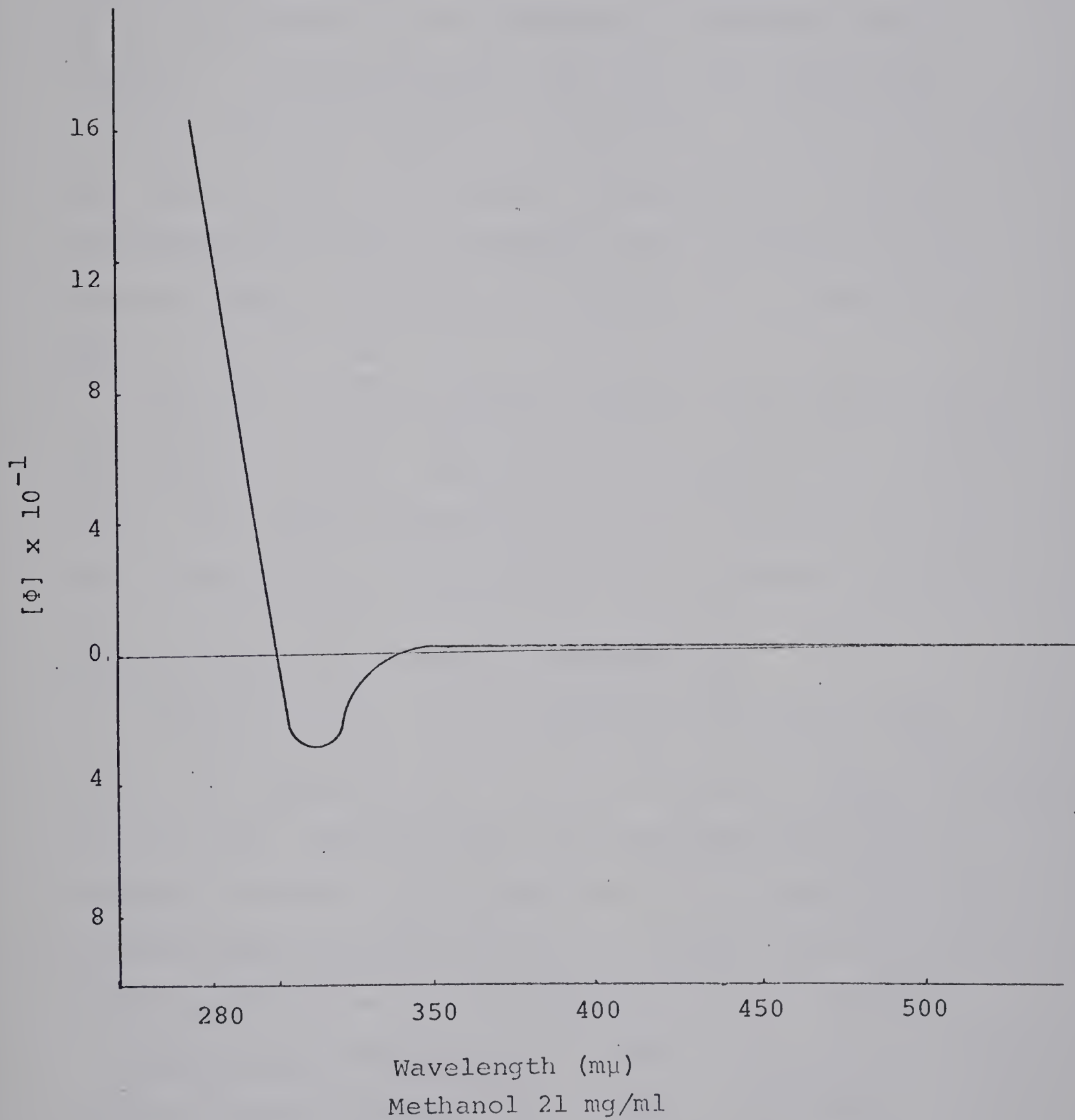


Figure 2. Optical rotatory dispersion curve of (-)-
16.

Preparation of 2-phenyl-1-butene, 20:

This olefin, one of the possible decomposition products of 7, was prepared by the sequence of reactions shown in Scheme 3. 2-Phenylbutanoic acid, 17, was reduced with lithium aluminium hydride. The alcohol, 2-phenyl-1-butanol, 18, was obtained in 83% yield. Acetylation of 18 by the acetylation procedure of Hammond (100) resulted in a 78% yield of ester. Pyrolysis of the acetate yielded 35% of 20.

The n.m.r. spectrum (CCl_4) showed a five proton phenyl absorption at $\tau 2.75$, two one proton singlets at $\tau 4.8$ and $\tau 5.0$, a two proton quartet ($J=7.5$ cps) centered at $\tau 7.5$, and a three proton triplet ($J=7.5$ cps) centered at $\tau 8.94$.

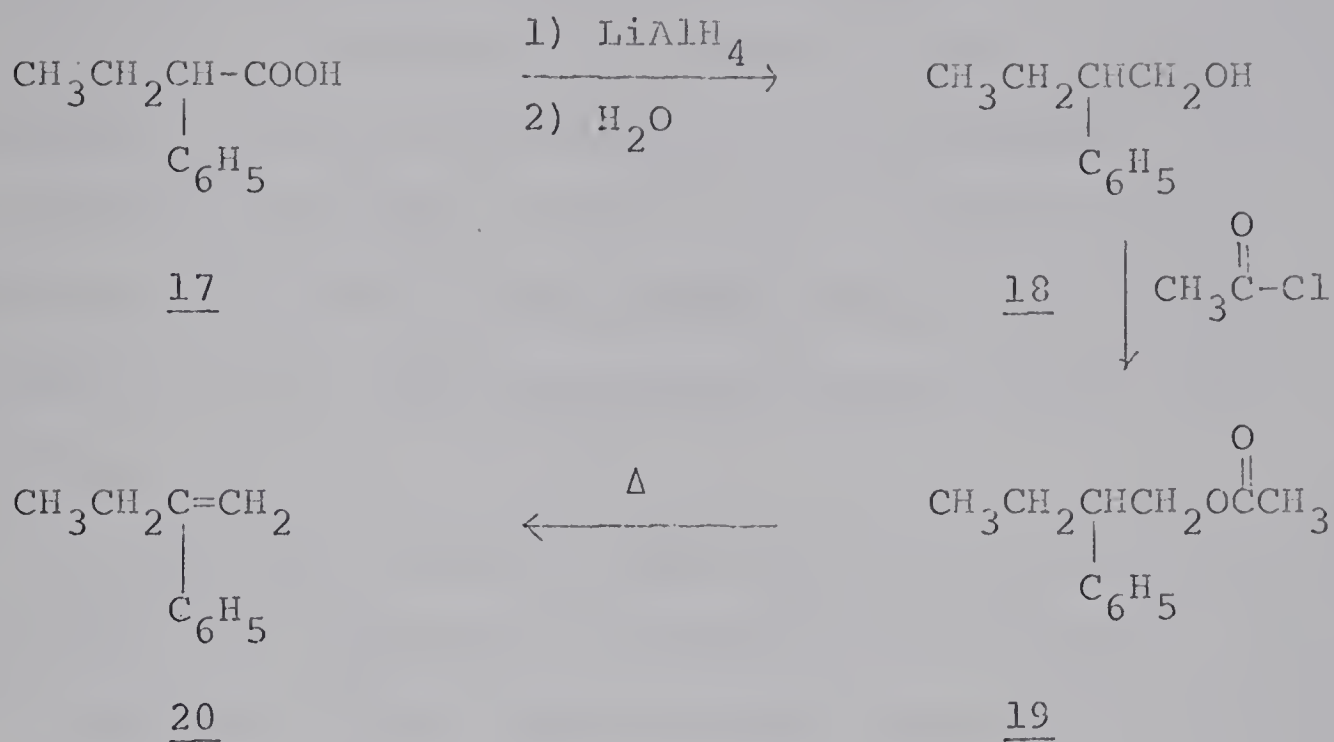
Preparation of cis-2-phenyl-2-butene, 22:

Another possible decomposition product of 7 is 22. Cram (104) reported a 4 : 1 ratio of cis- to trans-2-phenyl-2-butene was produced upon acid catalyzed dehydration of 2-phenyl-2-butanol, 21. Dehydration of 21 resulted in 3 olefins being produced as shown in Scheme 4 in the approximate amounts shown as estimated from g.l.c. analysis.

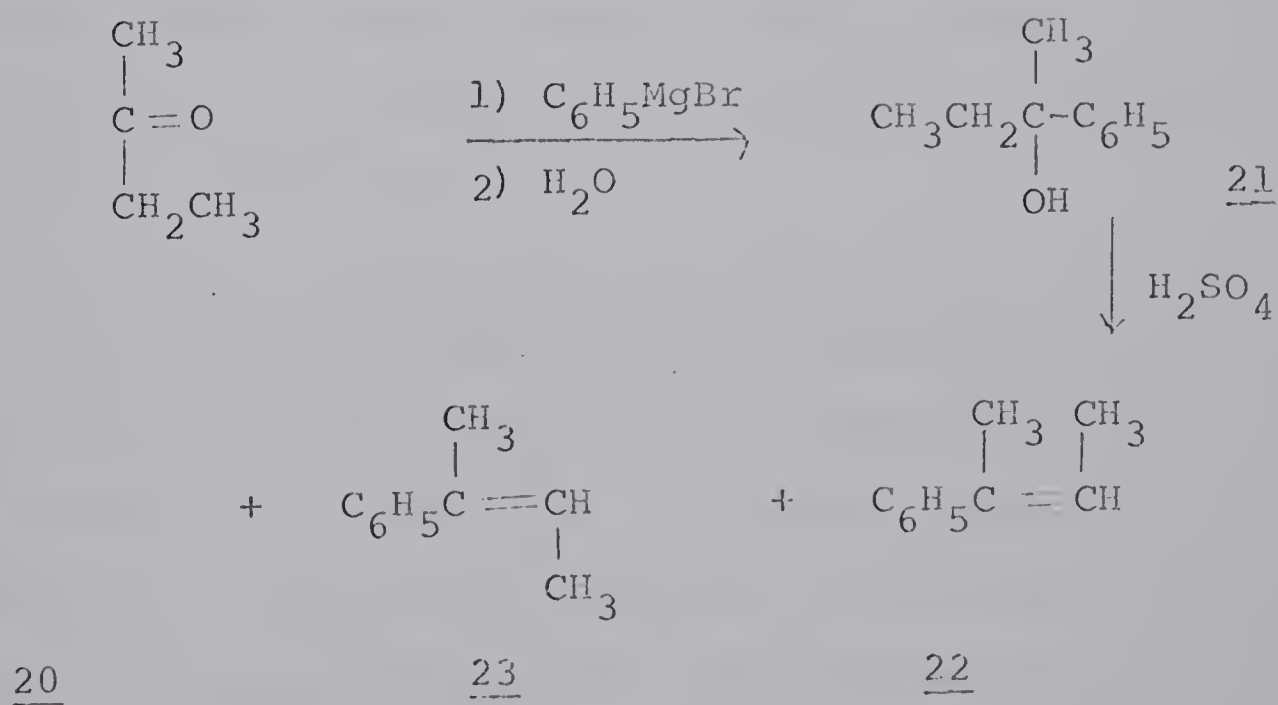
<u>cis</u> -2-phenyl-2-butene, <u>22</u>	70%	b.p. 194°
<u>trans</u> -2-phenyl-2-butene, <u>23</u>	5%	b.p. 174°
2-phenyl-1-butene, <u>20</u>	25%	b.p. 183°

After concentration of the olefin mixture, the highest

Scheme 3



Scheme 4



boiling fraction was distilled to give 22.

The n.m.r. spectrum (CCl_4) showed a five proton phenyl absorption at $\tau 2.78$, a one proton vinylic quartet ($J=6.5$ cps) centered at $\tau 4.13$, a three proton allylic methyl singlet at $\tau 8.0$, and a three proton doublet ($J=6.5$ cps) centered at $\tau 8.2$. The absorptions showed further fine structure.

The distillate obtained upon concentration of the olefin mixture was subjected to fractional distillation. The n.m.r. spectrum of the higher boiling fraction was identical to that of 2-phenyl-1-butene, 20. The lowest boiling compound was assumed to be trans-2-phenyl-2-butene, 23. Cram (104) has suggested that the interaction between a methyl and a phenyl group of the trans olefin 23 is greater than the interaction of two methyl groups of the cis olefin, 22. The greater stability of the cis olefin explains its predominance in the olefin dehydration mixture.

Preparation of 3,4-dimethyl-3,4-diphenylhexane, 24, 25:

The two symmetrical dimers of the 2-phenyl-2-butyl radical expected to arise from the decomposition of 7 were prepared by a di-tert.-butyl peroxide induced free radical coupling of 2-phenylbutane (105). The higher melting, m.p. 93° , less alcohol-soluble of the two dimers is the meso modification, 24 (105). The other low melting, m.p. $40-41^\circ$, dimer is the dl, 25 (105). An interesting feature of the

n.m.r. spectra of the two dimers is the two sets of methylene proton multiplets ($J=7$ cps) centered at $\tau 7.82$ and $\tau 8.50$. Since the methylene groups are adjacent to asymmetric centers, the methylene protons must experience different electric and magnetic effects. The two dimers had the same retention time on the gas-liquid chromatogram and could not be differentiated in this way.

Rate of decomposition of the azo compound, 7:

The rate of decomposition of the azo compound, 7, in cumene was determined by measuring the volume of gas evolved as a function of time. The rates were measured at 122.5° for approximately nine half-lives.

The rate constant, k_d , for this first-order decomposition is given by

$$k_d = \frac{2.303}{t} \log \frac{(V_\infty - V_0)}{(V_\infty - V_t)}$$

where

t = time

V_∞ = volume of gas evolved at infinite time

V_t = volume of gas evolved at time t

The initial readings of the volume of gas cannot be measured accurately due to the time required for the system to reach equilibrium. A graphical plot of $\log (V_\infty - V_t)$ versus time

was made and the slope is given by $-k_d/2.303$. From the slope of the plot, k_d was calculated. In the decomposition of 7 more gases than just nitrogen were evolved. At the temperature of decomposition propane, propylene and 2,3-dimethylbutane (all derived from the isopropyl radical) would be evolved. It was assumed that the total amount of gas would be proportional to the amount of azo compound decomposed. A typical rate data for the decomposition of 7 is given in Table I. A typical plot of $\log (V_\infty - V_t)$ versus time is shown in Figure 3. The half-life is calculated from the relationship

$$t_{\frac{1}{2}} = \frac{2.303}{k_d} \log 2 \quad (77)$$

The rate data are given in Table II. In Table III are presented the rate data and activation parameters obtained by Overberger (40) for the decomposition of a closely related azoalkane, 1,1'-dimethyl-1-phenylazoethane. The volume of gas collected in the gas burette was less than two equivalents. The solubility of any gases in water is not taken into account nor is the fraction of the isopropyl radical which couples to give a stable compound.

TABLE I

Typical Rate Data for the Decomposition of
1-Ethyl-1'-methyl-1-phenylazoethane, 7.

Temperature 122.5°

Solvent Cumene, Wt. of 7 0.102 g

Time seconds	Burette reading, ml	$(V_{\infty} - V_t)$	$\log(V_{\infty} - V_t)$	k_d (graphical) sec^{-1}
900	7.35	16.25	1.2108	
2100	9.47	13.06	1.1159	
3300	11.88	10.92	1.0382	
4500	13.62	9.18	0.9628	
5700	15.02	7.78	0.8910	
6300	15.82	6.98	0.8439	
7500	16.78	6.02	0.7796	
8700	17.75	5.05	0.7033	1.44×10^{-4}
9900	18.54	4.26	0.6294	sec^{-1}
11100	19.25	3.55	0.5502	
12300	19.98	2.82	0.4502	
13500	20.34	2.46	0.3909	
15300	20.95	1.85	0.2672	
16500	21.28	1.52	0.1818	
17700	21.40	1.40	0.1416	
18900	21.58	1.22	0.0864	
40500	22.80			

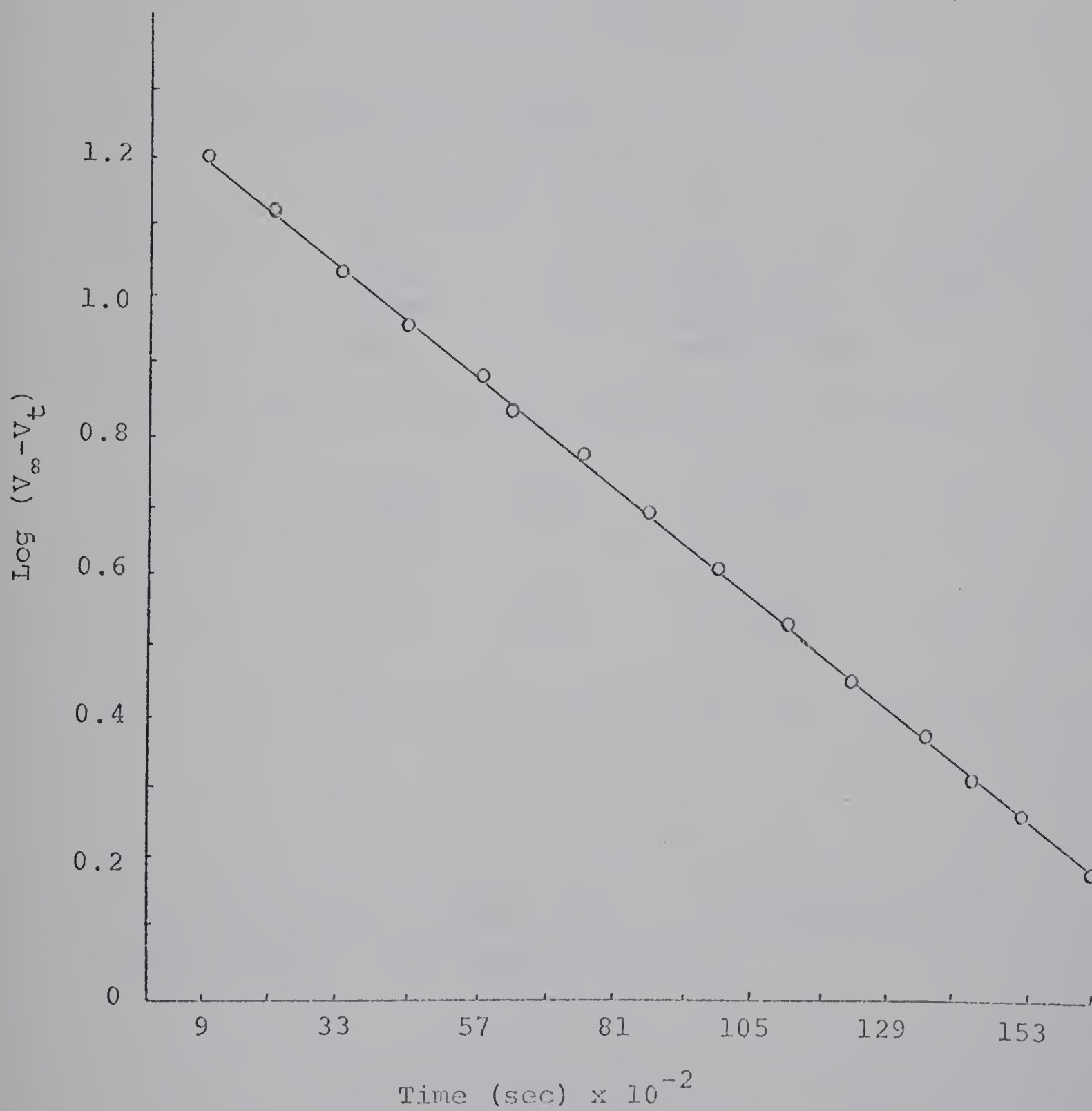


Figure 3. Plot of $\log (V_{\infty} - V_t)$ vs. time for gas evolution in the decomposition of 7.

TABLE II

The Rate Constant for the Decomposition of
1-Ethyl-1'-methyl-1-phenylazoethane

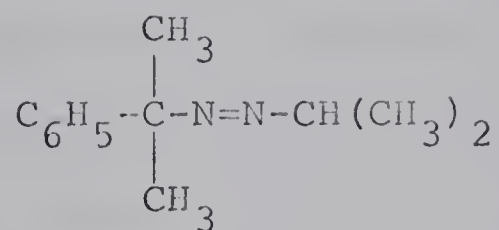
Cumene Solvent at 122.5°

Weight of <u>7</u> (g)	Gas Volume mls	% yield	Slope x 10 ³ from plot of log (V _∞ -V _t) versus time	k _d x10 ⁴ sec ⁻¹	t _{1/2} min.
0.102	22.80	85 ^a	0.0628	1.44	80
0.103	23.10	86 ^a	0.0642	1.48	78

^a
Calculated and corrected (STP) on the basis of two
equivalents of gas being evolved.

TABLE III

Data of Overberger (40) for the Decomposition of
1,1'-Dimethyl-1-phenylazoethane



<u>Temperature</u>		<u>$k \times 10^4 \text{ sec}^{-1}$</u>
120°		1.06
125°		1.95
135°		5.94
143°		14.21
at 120°	E_A	36.7 kcal/mole
	ΔS^\ddagger	14 cal/mole degree

Product analysis of the decomposition of 7:

Approximately 10% 7 in benzene was decomposed in degassed and sealed tubes. The reaction mixture of all sealed tube decompositions was chromatographed on neutral alumina prior to analysis. It was necessary to chromatograph the mixture in order to remove hydrazone which was produced during the decomposition by isomerization of the azo compound, 7. The hydrocarbon decomposition products are less polar than the hydrazone and are preferentially eluted from the column. Under the g.l.c. conditions used for the analysis, the hydrazone, if not removed, gave a very broad peak at the same retention time as that of the unsymmetrical coupling product, 16.

In the scavenged runs dibutyl disulfide, dimerized butyl thiyl, had almost the same retention time as the unsymmetrical coupling product. By decreasing the rate of column temperature increase, the two peaks could be sufficiently separated to enable an estimate to be made of the area of the peak corresponding to the coupling product, 16.

The product analysis was concerned only with the fate of the 2-phenyl-2-butyl radical. No analysis was performed for propane, propylene, and 2,3-dimethylbutane. Meso- and dl-3,4-dimethyl-3,4-diphenylhexane could not be distinguished on the column and conditions employed. No para coupling product, 1-(2-butyl)-4-(2-propyl)-benzene, 26,

or trans-2-phenyl-2-butene, 23, were detected. In all determinations only between 50 and 60% of the 2-phenyl-2-butyl radical in the form of derived products could be accounted for. Table IV summarizes the results obtained during unscavenged azo decompositions. Table V summarizes the results obtained with butanethiol scavenged azo decompositions.

Preparation of 1-(2-butyl)-4-(2-propyl)-benzene, 26:

1-(2-Butyl)-4-(2-propyl)-benzene was suspected to be one of the decomposition products of 7. It was synthesized from 2-phenylbutane and 2-propyl chloride and the common Friedel-Craft catalyst, aluminium chloride. Based on g.l.c. analysis, at least nine compounds formed from the reaction. The major peak of the mixture had a very similar retention time to that of the unsymmetrical coupling product, 16, of the decomposition of azo compound 7. Since there were unidentified peaks on the gas chromatogram occurring near 16, compound 26 was considered as a likely possibility. Compound 26 was collected from the effluent of the gas chromatograph. The most indicative proof that the proper alkylated product was isolated was the sharp absorption at 825 cm^{-1} (para di-substituted benzene) in the infrared spectrum (CCl_4).

TABLE IV

Relative Product Distribution of Unscavenged
Thermal Decomposition of 1-Ethyl-1'-methyl-1-
phenylazoethane at 100° and 125°

Benzene solvent

		Product proportions ^a					
		mole percent				2-phenyl- butane	%
	2-phenyl- butane	<u>20</u>	<u>22</u>	<u>16</u>	<u>24,25</u>	<u>16</u>	recovery
<hr/>							
100°							
run 1	23	2	2	59	14	0.39	50
run 2	23	2	3	58	13	0.40	52
average	23	2	3	59	14	0.40	
125°							
run 1	21	1	2	59	17	0.36	51
run 2	21	1	2	57	17	0.37	54
average	21	1	2	58	17	0.37	

^a Product analysis by g.l.c. on SF96 column, temperature
programmed. Analysis was done in quadruplicate.

TABLE V

Relative Product Distribution of 1 M Butanethiol
Scavenged Thermal Decomposition of 1-Ethyl-1'-
methyl-1-phenylazoethane at 100° and 125°.

Benzene solvent

	2-phenyl- butane	<u>16</u>	2-phenyl- butane <u>16</u>	% recovery
<u>100°</u>				
run 1	64	36	1.78	59
run 2	63	36	1.74	55
average	64	36	1.76	
<u>125°</u>				
run 1	73	27	2.73	57

^aProduct analysis by g.l.c. on SF96 column, temperature
programmed. Analysis was done in quadruplicate.

Decomposition of (+)-7:

The decomposition of (+)-7, $\alpha_D^{25} +35.5^\circ$ (1 1 dm., neat), was carried out in benzene and chlorobenzene (1 M with respect to butanethiol) solutions in a stainless steel pressure bomb. After at least ten half-lives, the bomb was removed from the preheated oven. The solution was concentrated and then reacted with trichlorosulphenyl chloride (111) to remove traces of olefin. The crude product after work-up was chromatographed on activated basic alumina in a water-cooled and jacketed column. Sufficient alumina was used to adsorb the dibutyl disulfide. The two hydrocarbons of interest, 2-phenylbutane and 2,3-dimethyl-3-phenylpentane, 16, were collected from the effluent of the gas chromatograph. Compound 16 was analyzed for optical activity by o.r.d. The molecular rotation, $[\Phi]$, at 280 m μ was compared to $[\Phi]_{280}$ of authentic and 97% optically pure (-)-16 to get an estimate of optical activity. Figure 4 shows the o.r.d. curve obtained for 16 from the decomposition of (+)-7 in 1 M butanethiol in benzene at 100°. Figure 5 shows the o.r.d. curve obtained for 16 from the scavenged decomposition of (+)-7 in chlorobenzene at 125°. Table VI shows the molecular rotation, $[\Phi]_{280}$, obtained from Figures 4 and 5 as well as the isolated yields of the two hydrocarbons.

Calculated rotation of (S)-(-)-2,3-dimethyl-3-phenylpentane:

The observed rotation of (-)-16 was disappointingly

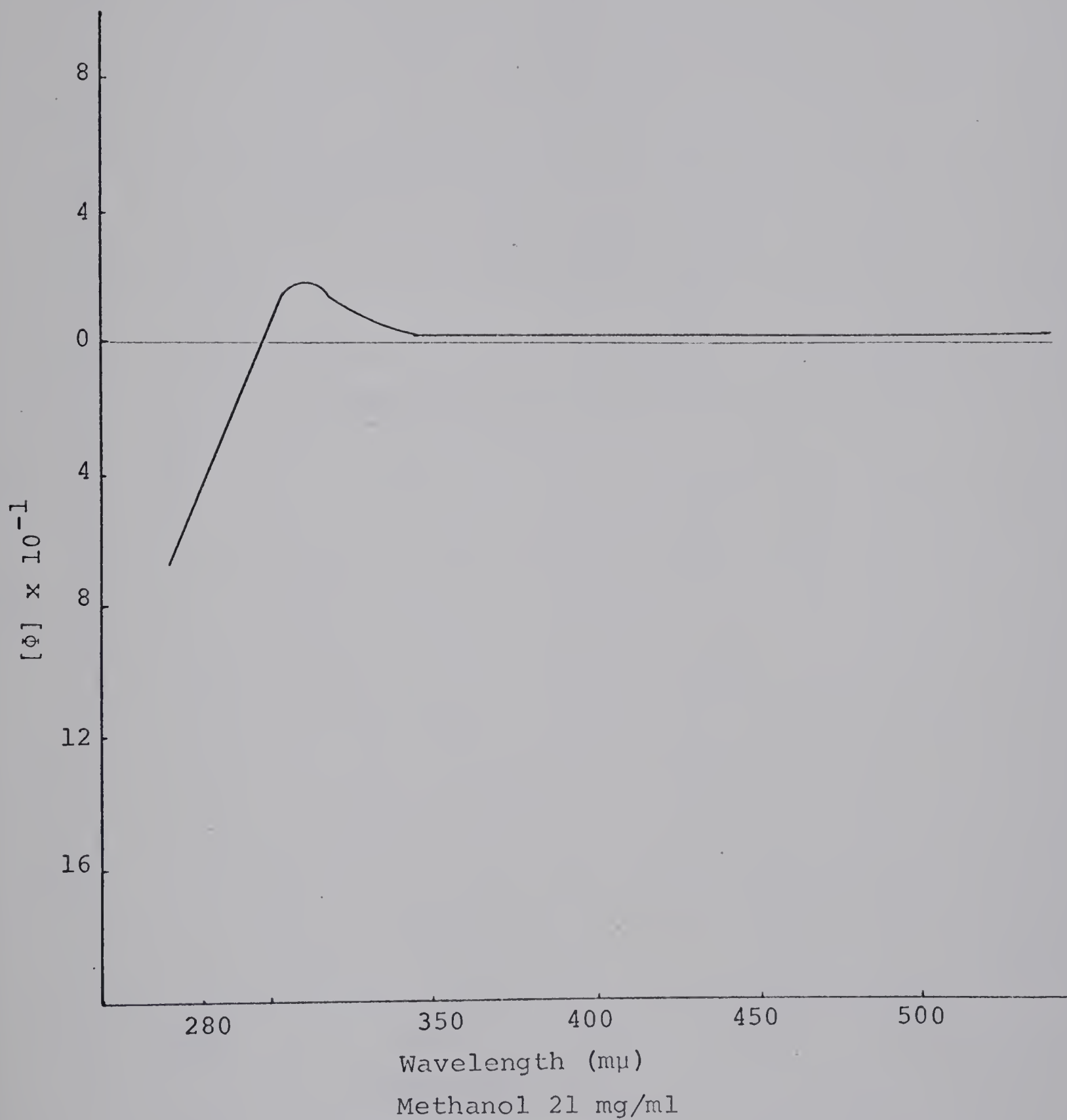


Figure 4. Optical rotatory dispersion curve of (+)-16 obtained from scavenged decomposition of (+)-7 in benzene at 100°.

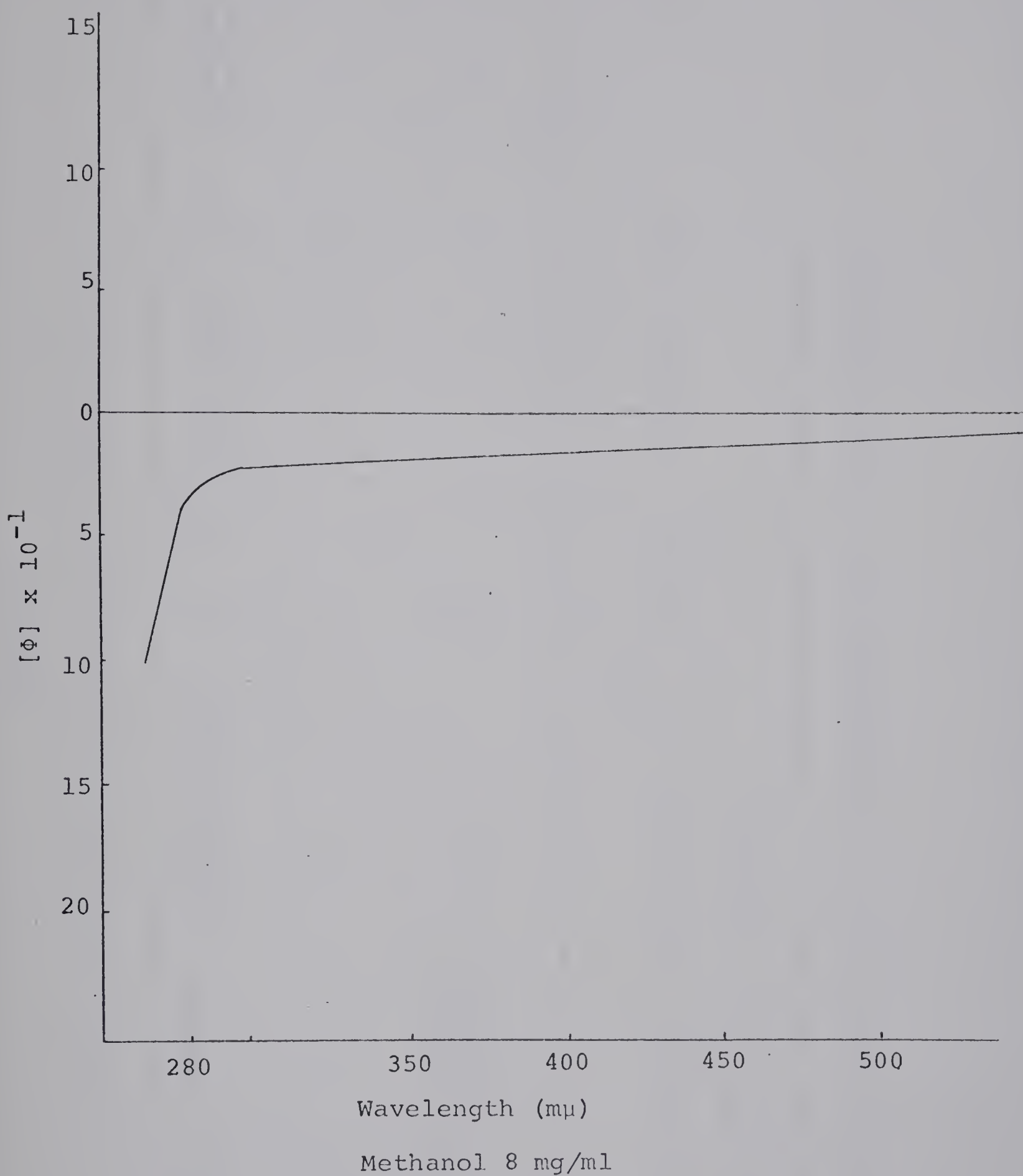


Figure 5. Optical rotatory dispersion curve of (+)-16 obtained from scavenged decomposition of (+)-7 in chlorobenzene at 125°.

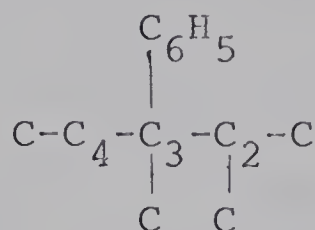
TABLE VI

Rotation and Yields of Decomposition Products of (+)-7

°C	wt. 7 (g)	Solvent	isolated wt. (mg) 2-phenylbutane	<u>16</u>	α_D^{25} (<u>16</u> dm, neat) 2-phenylbutane	$[\phi]_{280}^{16}$	Estimated a retention
100°	1.842	benzene ^b	192	41 ^c	-0.28°	-37°	41%
125°	1.812	chloro- benzene	43	8 ^d		-15°	17%

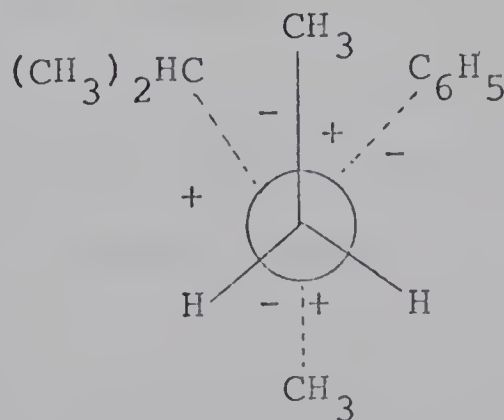
^aBased on $[\phi]_{280}$ recovered 16authentic (-)-16.^bSolvents were 1 M in butanethiol.^cConcentration used for o.r.d. determination was 21 mg/2ml methanol.^dConcentration used for o.r.d. determination was 8 mg/ml methanol.

low, $\alpha_D^{25} -4.0^\circ$ (1 l dm., neat). There is no known mechanism to account for racemization during the hydrogenation of (+)-2,3-dimethyl-3-phenyl-1-pentene, (+)-15, $\alpha_D^{25} +11.3^\circ$ (1 l dm., neat), to (-)-2,3-dimethyl-3-phenylpentane. The optical activity of (S)-16 was calculated using the rules developed by Brewster (78). Rotation about two bonds was considered in this calculation, C_2-C_3 and C_3-C_4 .



All alkyl groups are assumed to have the same polarizability as the methyl group. To represent interactions between the various groups, C represents an alkyl group, P a phenyl group and H a hydrogen.

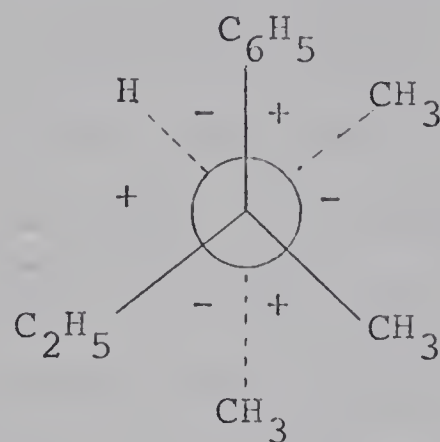
One of the three possible conformations of (S)-16 looking along the C_4C_3 bond is



The group interactions for this conformation are

+CP	-PH
+CH	-CH
+CH	-CC

Using the conformation given above and looking along the C_3-C_2 bond, one of three possible conformations is



The group interactions for this conformation are

+CP	-CC
+CC	-CC
+CH	-PH

The algebraic summation of the group interactions of the two conformations considered above is $2(PC-PH+CH-CC)$. Factoring this expression gives $2(C-H)(P-C)$ which is the form of the equation used by Brewster to calculate the conformational rotatory powers from the substituent polarizabilities.

There are a total of nine possible conformational pairs to be considered. Of the nine, four were discarded after model inspection because they violated one of Brewster's

empirical rules, rule two. Algebraic summation of the group interactions of the accepted conformational pairs gives the following equation for the molecular rotation:

$$[M] = \frac{k(C-H) [3(C-P) + 2(P-C)]}{5}$$

The conformational rotatory power is calculated from the equation $160(R_C^{\frac{1}{2}} - R_H^{\frac{1}{2}})(R_A^{\frac{1}{2}} - R_H^{\frac{1}{2}})$, where R is the polarizability of the given substituent, and A in this example would be the phenyl group. If the polarizability of the phenyl group is taken as 6.757 (78), the value which gives the more accurate estimations of optical activity in many systems, the calculated molecular rotation of (S)-(-)-2,3-dimethyl-3-phenylpentane is -19.2° . If the generally less accurate phenyl polarizability of 3.379 (78) is taken, the calculated molecular rotation is -4.4° . To convert molecular rotation to α , the observed rotation, the following formulae were used

$$[M] = \frac{[\alpha]_D M}{100}$$

$$[\alpha]_D = \frac{\alpha}{\rho}$$

where

[M] = molecular rotation

M = molecular weight

α = observed rotation (1 1 dm., neat)

$[\alpha]_D$ = specific rotation

ρ = density (estimated to be 0.87)

On this basis from the polarizability of 6.757, the observed rotation would be -9.5° and from the polarizability of 3.379, the observed rotation would be -2.2° . An encouraging feature of the calculation is the correct sign of rotation. The observed magnitude of rotation is, however, considerably lower than calculated.

D I S C U S S I O N

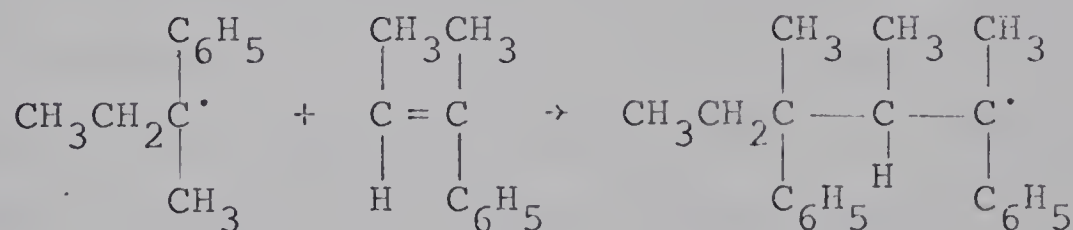
Aliphatic azo compounds are conveniently synthesized by oxidative coupling of tertiary-substituted primary amines by iodine pentafluoride (79). This method has been utilized to synthesize optically active symmetrical aliphatic azo compounds (25,114). The synthetic route to aliphatic unsymmetrically substituted azoalkanes entails a multi-step sequence. The general method of Overberger (90) is the more common route to these compounds. There has been no published preparation of an optically active unsymmetrical azo compound although an enantiomer of 1,1'-diphenyl-1-methylazomethane has been isolated (80).

In this work (+)-1-ethyl-1'-methyl-1-phenylazoethane was prepared. The general method of Overberger (90) was employed. The hydrazine, N-(2-propyl)-N'-2-phenyl-2-butylhydrazine, was resolved as the dibenzoyl tartrate. Two recrystallizations of the salt and subsequent oxidation of the hydrazine yielded the unsymmetrical azoalkane, (+)-7, 84% optically pure.

The decomposition of the azo compound, 1-ethyl-1'-methyl-1-phenylazoethane, has been shown to follow first order kinetics. At 122.5° the observed rate constant was $1.44 \times 10^{-4} \text{ sec}^{-1}$ and the half-life was 80 minutes. Compound 7 evolved nitrogen as well as propane and propylene upon decomposition. The graphically obtained rate is

qualitatively comparable to the rate of the decomposition of 1,1'-dimethyl-1-phenylazoethane (40) shown in Table III. Such similarity in the rate of decomposition is expected since there is very little structural difference between the two azoalkanes.

In the product analysis determinations only 50 to 60% of the 2-phenyl-2-butyl radical derived products could be accounted for. Only "normal" products were sought, that is, only those products expected from direct combination of two different radicals, dimerization, or disproportionation. Those products which could conceivably arise from radical addition to a formed product were not considered. For example:



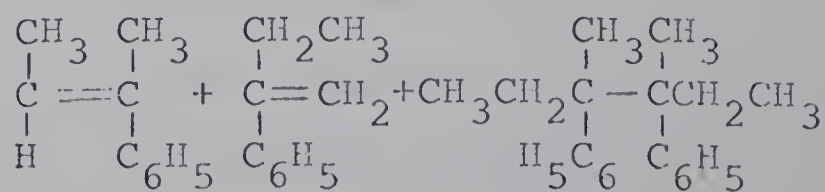
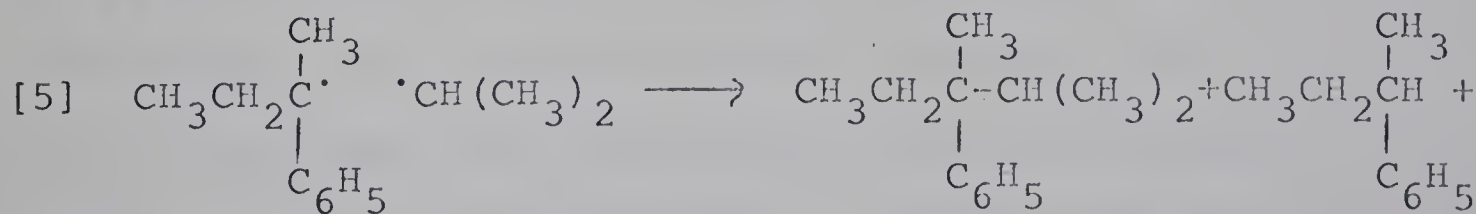
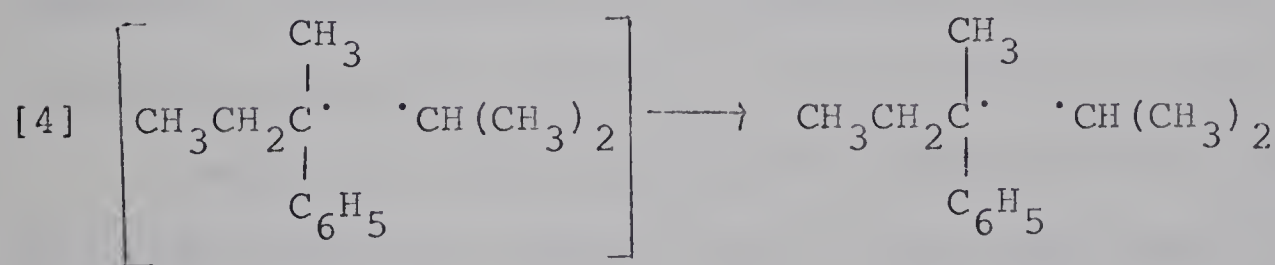
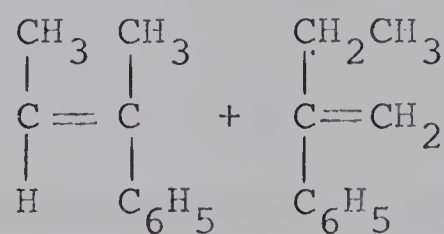
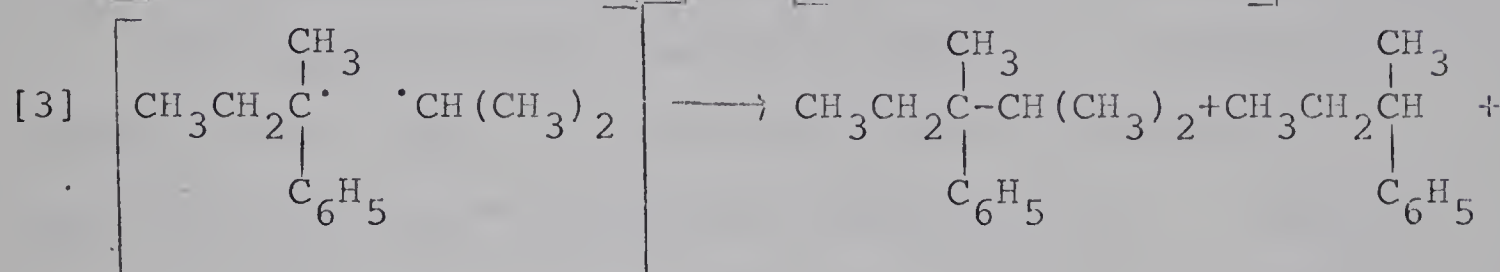
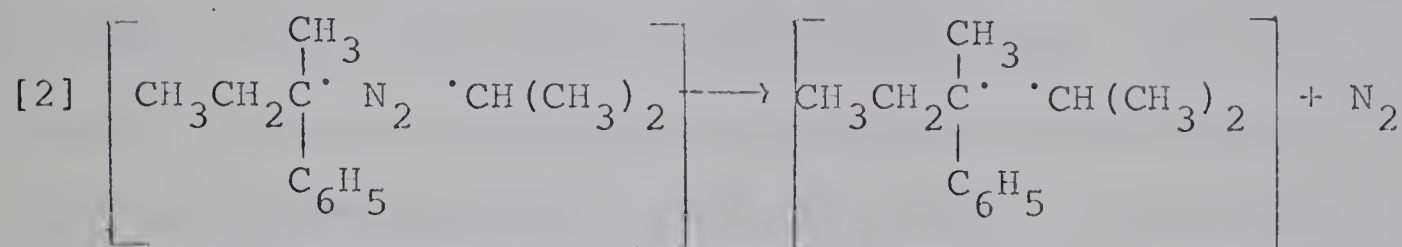
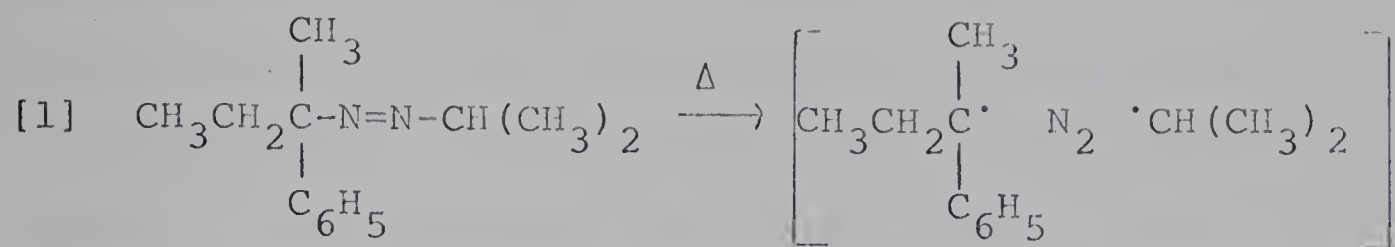
There were peaks on the gas-liquid chromatogram which were not identified and which were suspected to be formed from the 2-phenyl-2-butyl radical. Table IV shows that about 5% of the total products was olefin. If the olefins arise only from disproportionation with an isopropyl radical or another 2-phenyl-2-butyl radical, then an equal amount of 2-phenylbutane would also be expected. Since the amount of 2-phenylbutane is approximately 5 times that of

total olefin, it seems that some olefins formed are consumed.

A second reason for the material imbalance is isomerization of the azo compound to the hydrazone. Hydrazone was shown to be present in the azo decomposition product mixture. Under the conditions of the decomposition, hydrazone decomposes at a slower rate than does the azo compound. The extent of isomerization could not be determined from ultraviolet spectroscopy because the absorption maximum of the hydrazone is near 230 mμ which is also the region of absorption of the benzene solvent used.

The thermal decomposition of 7 is depicted in Scheme 5. The initially formed radicals may undergo reaction in the cage [3] or they may diffuse out of the cage and then undergo coupling and disproportionation [5]. In the presence of added scavenger only those products shown in equation [3] will be formed. In Scheme 5 only the expected products from the 2-phenyl-2-butyl radical are shown. The mole percent product proportions of unscavenged decomposition are shown in Table IV. No significant variation of the amounts of disproportionation and combination were observed at the two temperatures of decomposition. Bartlett (20) has reported that the ratio of disproportionation to combination does not vary with temperature. He attributed similar activation energies for the two processes. In the presence of

Scheme 5



meso and dl

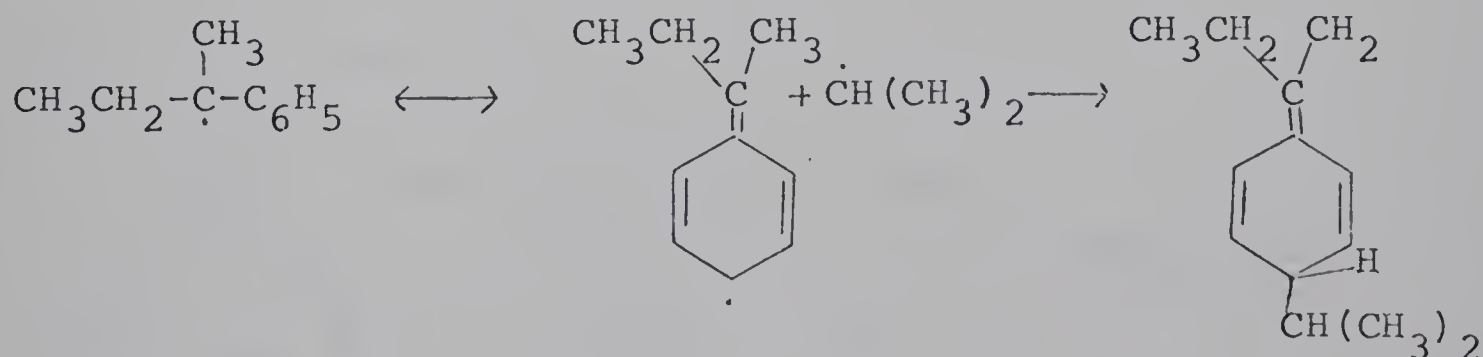
butanethiol scavenger dimerization of the 2-phenyl-2-butyl radical is completely prevented and the amount of detected olefin is negligible. The results are shown in Table V. It is possible that butyl thiyl radicals add to the olefin and form an addition product. The 2-phenylbutane produced inside the cage cannot be differentiated from the 2-phenylbutane produced outside the solvent cage.

The unsymmetrical coupling product, 2,3-dimethyl-3-phenylpentane, 16, and 2-phenylbutane are produced in both scavenged and unscavenged decompositions. 2-Phenylbutane is formed whenever the 2-phenyl-2-butyl radical abstracts a hydrogen atom. Compound 16 will be formed both inside and outside of the solvent cage in an unscavenged decomposition. In a scavenged decomposition, the 2,3-dimethyl-3-phenylpentane is formed as a result of primary and unscavengeable secondary recombinations in the cage.

Under the conditions of the experiment the amount of disproportionation taking place in the cage could not be calculated. All 2-phenyl-2-butyl radicals which diffused out of the cage would be scavenged by the butanethiol and would appear as 2-phenylbutane. Olefins formed in the cage could react with thiyl radicals to form addition compounds. Only the direct coupling product, 2,3-dimethyl-3-phenylpentane, is solely a cage-produced product which was analyzed. The mole percent of the coupling product is shown in Table V. The values of this compound, 38% at 100° and 27% at

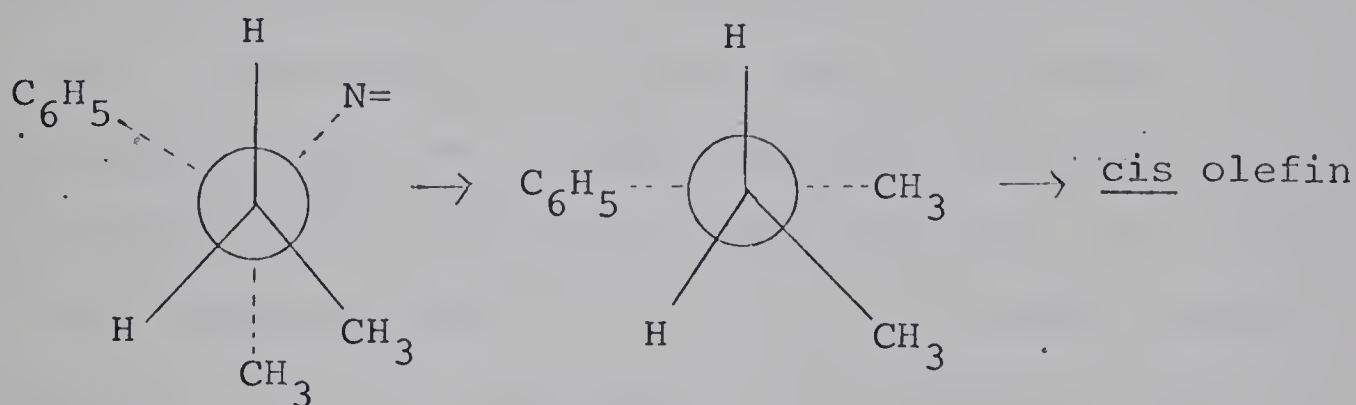
125°, represent the lower limits of the cage effect. The cage effect reported here is higher than that estimated by Bartlett (21) of 28% at 40° for the thermal decomposition of azocumene in toluene. Percent cage effect is inversely related to the temperature of decomposition (21). At 100° Bartlett's cage effect would be much lower. Solvent viscosity is inversely related to temperature (26). The cage effect has been shown to vary directly with viscosity (28). The higher estimated cage effect at 100° than at 125° is, therefore, reasonable.

Bartlett has published some ultraviolet spectroscopic evidence for a para coupling product. He was unable to isolate this material. Pryor (29) has isolated a para coupled cage product in the decomposition of p-nitrophenylazotriphenylmethane. Such a para coupling product was sought in this investigation.

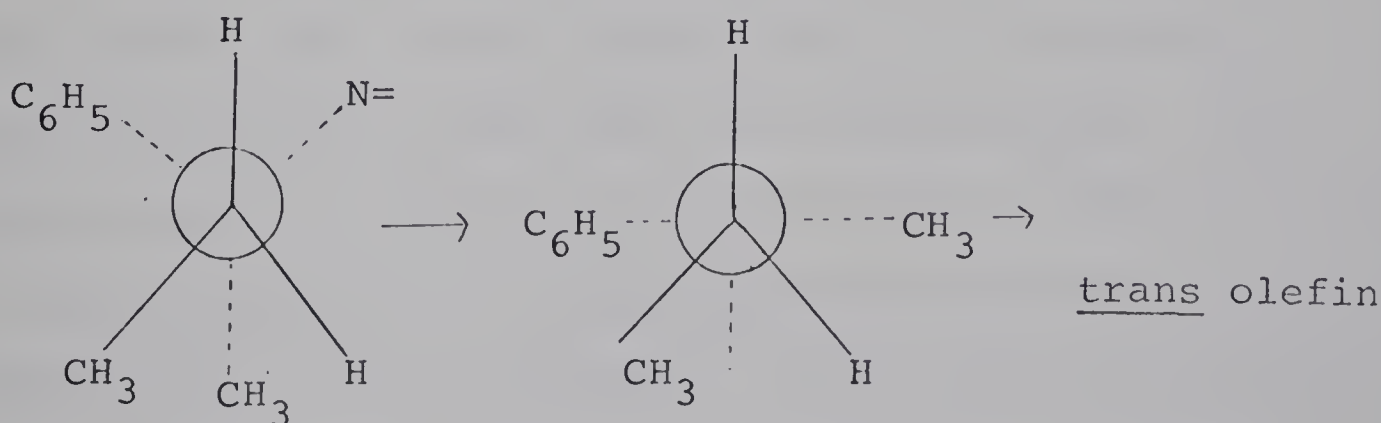


If such a species were formed, it would aromatize readily. No 1-(2-butyl)-4-(2-propyl)-benzene was detected in the azo decomposition mixture.

An interesting side-light of the relative product distribution of the unscavenged azo decomposition was the absence of detectable amounts of trans-2-phenyl-2-butene. Cram (104) has suggested that cis-2-phenyl-2-butene is more thermodynamically stable than the trans olefin due to steric reasons. The transition state leading to formation of the cis olefin has a methyl-methyl interaction.



This interaction must be more favourable than the methyl-phenyl interaction of the transition state leading to trans olefin.



The 2-phenyl-2-butyl radical also disproportionated to give 2-phenyl-1-butene. This olefin resulted from the abstraction of one of the three primary hydrogens of the

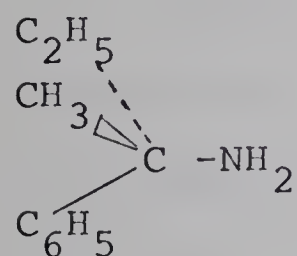
methyl group. Such a process must be competitive with abstraction of a secondary hydrogen from a methylene group.

Bartlett (25) has shown that free radicals are able to retain enantiomeric integrity in the solvent cage in the frozen state at 77°K. He has reported the photolysis of meso and dl isomers of azo-bis-3-methyl-2-phenyl-2-butane in the frozen state. Only meso and dl dimers, respectively, were isolated. At higher temperatures (0° to 100°) stereospecificity was lost. Walborsky (67) has published a report of a cage disproportionation reaction proceeding with retention of configuration. The results of the decomposition of (+)-1-ethyl-1'-methyl-1-phenyl-azoethane, (+)-7, in butanethiol are shown in Table VI. Both 2-phenylbutane and 2,3-dimethyl-3-phenylpentane, 16, show optical activity. Since the azo compound decomposes by a two bond cleavage (34) and since 16 is formed only in the solvent cage, these figures measure retention of optical activity in the geminate recombinations. The optical activity shown by 2-phenylbutane in the run at 100° is due to retention in cage disproportionation. It is unlikely that a 2-phenyl-2-butyl radical which has diffused out of its solvent cage would upon hydrogen abstraction from butanethiol yield an optically active product.

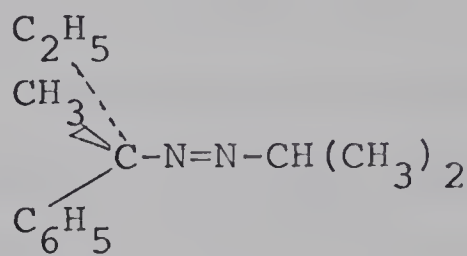
The optical activity of 16 was estimated by o.r.d. The molecular rotation at 280 mμ of the isolated coupling products was computed (74) and compared to the molecular

rotation of optically pure (-)-16. The ratio calculated is used as an estimate of retention of optical activity in the cage. The molecular rotation at 280 mμ is reproducible to within 5%. Molecular rotations at other wavelengths are not too satisfactorily reproduced. The estimated retention of optical activity in the cage is comparable in magnitude to the estimated cage effect based upon product analysis.

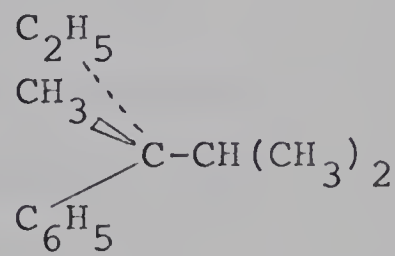
There is net retention of configuration of the two hydrocarbons produced in the cage. Hydrogenolysis of (+)-7 gave (-)-27. Cram (91) has shown that the acid, (+)-11, has the same absolute configuration as (-)-27. In this investigation (-)-11 was converted to (+)-15. The olefin, (+)-15 was hydrogenated to (-)-16. The azo compound, (+)-7,



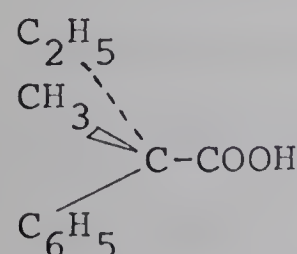
(-)-27, $\alpha_D^{25} -16.8^\circ$
(1 1 dm., neat)



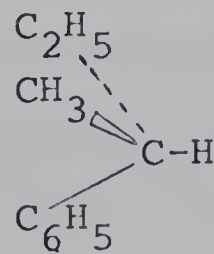
(+)-7, $\alpha_D^{25} +42.2^\circ$
(1 1 dm., neat)



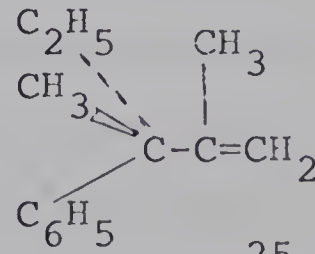
(+)-16, $\alpha_D^{25} +0.4^\circ$
(1 1 dm., neat)



(+)-11, $[\alpha]_D^{25} +30.2^\circ$
(c 4.8, benzene)



(-)-2-phenylbutane
 $\alpha_D^{25} -24.3^\circ$ (1 1 dm., (1 1 dm., neat)
neat)



(-)-15, $\alpha_D^{25} -11.7^\circ$

was hydrogenolyzed to (-)-27 and decomposed to (+)-16.

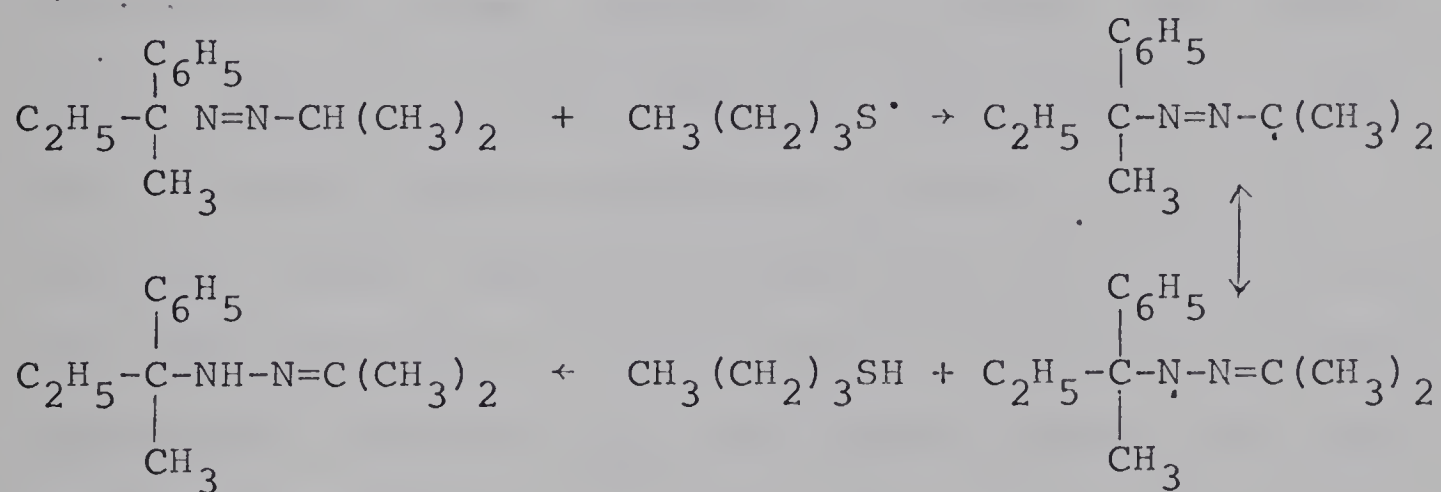
Since (-)-27 has the same absolute configuration as (+)-11, and since (+)-11 has the same absolute configuration as (+)-16, (-)-27 and (+)-16 belong to the same series. (+)-2-Methyl-2-phenylbutanoic, (+)-11, has the same absolute configuration as (-)-2-phenylbutane (81) and (+)-7. As a result there is retention of configuration of the products derived from 2-phenyl-2-butyl radical in the cage.

(+)-2-Methyl-2-phenylbutanoic acid, (+)-11, has the same absolute configuration as (-)-2-phenylbutane (82). Cram (83) has shown that (-)-2-phenylbutane has the "R" arrangement related to that of D-glyceraldehyde. The (-)-2-methyl-2-phenylbutanoic acid must have the "R" arrangement also. The unsymmetrical coupling product, 2,3-dimethyl-3-phenylpentane, (-)-16, synthesized from (-)-2-methyl-2-phenylbutanoic acid must have the "S" arrangement.

Under the experimental conditions used it is not possible to quantitatively determine the relative amounts of 2-phenylbutane formed inside and outside of the solvent cage. As a result it is not possible to predict what percentage of retention of configuration for the cage disproportionation the 1% optical activity of the isolated 2-phenylbutane represents.

The low yield of optically active hydrocarbons

isolated from the thermal decomposition of (+)-7 is difficult to rationalize. Isomerization of the azo compound is a very likely process. Bickel and Kooyman (84) have decomposed 1,1'-diphenyl-azo-bis-ethane at 125° in inert solvents and in the presence of 2 molar n-octyl mercaptan or thiophenol. With a scavenger present there was a 42% reduction of nitrogen evolved as well as the concomitant formation of acetophenoneazine and ethylbenzene. Isomerization of (+)-7 could occur in an analogous manner,

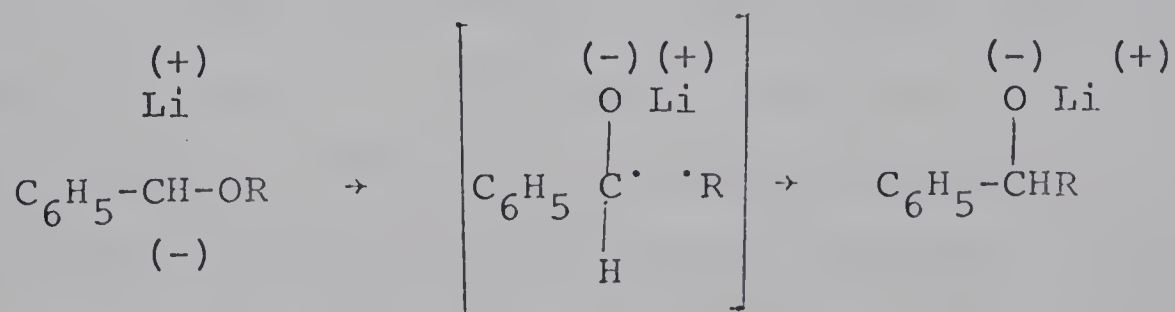


The fact that there is retention of configuration of the hydrocarbons formed in the solvent cage does not necessarily imply that the intermediate 2-phenyl-2-butyl radical retains its pyramidal geometry. It is possible that the 2-phenyl-2-butyl radical assumes a planar form. Coupling with the geminately formed isopropyl radical will occur from the same face of the 2-phenyl-2-butyl radical as that where the carbon-nitrogen bond was homolytically cleaved. The result is net retention of configuration.

Intervening solvent molecules greatly decrease the probability of a back-side coupling to give net inversion with an isopropyl radical produced by a neighbouring azo molecule decomposition.

If butanethiol scavenged all non-cage restrained 2-phenyl-2-butyl radicals, it is interesting to speculate why there was not complete retention of optical activity of the hydrocarbons. Perhaps retention of configuration occurs only during primary recombinations. Secondary recombinations occur, according to solvent cage theory (2,3), after one or two diffusive displacements. This time interval may be sufficiently long to permit the 2-phenyl-2-butyl radical to turn about prior to coupling with the geminately formed isopropyl radical but before scavenging. Rotation may, to a small extent, also compete with coupling.

If the Wittig rearrangement is exclusively a free radical rearrangement, then tertiary ethers rearrange with 80% retention of configuration in the solvent cage (66).



This large value is not unreasonable. Essentially it is

only a 1,2 rearrangement. The radicals formed are very close together and undergo primary recombination. The close proximity of the radical to the Cr^{V} could also account for the high retention of configuration in chromic acid oxidation of tertiary hydrocarbons (69). In (+)-1-ethyl-1'-methyl-1-phenylazoethane, (+)-7, the two radicals are at least a nitrogen molecule diameter apart when they are first formed. As a result the geminate radicals are further apart than those in the Wittig rearrangement solvent cage. The azo produced radicals may undergo a lesser amount of primary recombination. If optical activity results solely from primary recombinations, the overall net retention of configuration will be lower than that observed by Schollkopf (66) and Wiberg (69). The estimates of retention of configuration in Table VI may well be estimates of primary recombination.

The optical activity of (-)-2,3-dimethyl-3-phenylpentane, $\alpha_{\text{D}}^{25} -0.4^{\circ}$ (1 1 dm., neat), was not a priori anticipated to be so low. Wynberg (85) has prepared an asymmetric tetra-alkylmethane which showed essentially no optical rotation. The phenyl substituent of (-)-16 has sufficiently different polarizability (78) from an alkyl group and should cause optical activity. The analogous compound where hydrogen is substituted for a phenyl group, 2,3-dimethylpentane, is reported to have

$[\alpha]_D^{20} -11.4^\circ$ (86). In some classes of compounds the presence of a phenyl group enhances the optical activity. Lactic acid is reported to have $[\alpha]_D^{15} +3.82^\circ$ (water) (87). The phenyl-substituted lactic acid, atrolactic acid, is reported to have $[\alpha]_D^{15} -53.8^\circ$ (water) (88).

Calculating the observed rotation of (S)-(-)-2,3-dimethyl-3-phenylpentane from Brewster's empirical rules (78), values of -9.5° and -2.2° were obtained. The value -9.5° was obtained by using the higher polarizability value of the phenyl group (78). The higher polarizability value has been found to give the more accurate estimates of optical activity in many systems.

Thomson (89) found that his empirical quantitative relationship rules for calculating molecular rotations from structure gave erroneous results for compounds having an isopropyl group attached to the asymmetric center. Rotations of compounds with isopropyl groups attached to the asymmetric center are known to fall out of line with rotations of homologous series (89). The isopropyl group of (-)-16 could well be the cause of its unexpectedly low optical rotation.

E X P E R I M E N T A L

Physical measurements:

All boiling points and melting points reported are uncorrected values. Melting points were taken on a Gallenkamp melting point apparatus.

Infrared spectra were recorded on a Perkin-Elmer Recording Infrared Spectrophotometer, Model 421 or Model 337.

Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian Analytical Spectrophotometer, Model A-60. Tetramethylsilane (TMS) was used as the internal reference.

Neat optical rotations were taken on a Rudolph Polarimeter, Model 80, No. 727. Solution optical rotations were taken on a Perkin-Elmer 141 Polarimeter. Optical rotatory dispersion (o.r.d.) curves were taken on a Model ORD/UV-5 Japan Spectroscopic Company spectropolarimeter.

Ultraviolet spectra were taken on a Bausch and Lomb Spectronic 600 Spectrophotometer.

Indices of refraction were measured on a Bausch and Lomb Abbe-3L Refractometer.

Gas-liquid chromatography (g.l.c.) was done on an Aerograph 202 fractometer with a Honeywell recorder. A 6 ft x $\frac{1}{4}$ inch stainless steel tubing was packed with 20% SF96 on Chromosorb W and served as the column. This

instrument was used for both analytical and preparative gas chromatography. Helium was the carrier gas.

Purification of chlorobenzene:

Commercially obtained mono-chlorobenzene (Fisher) was purified by successive washing with three portions of concentrated sulfuric acid, with two portions of water, and finally with two portions of saturated sodium bicarbonate. After drying over magnesium sulfate, the solvent was distilled from phosphorus pentoxide through a 4-foot Podbielniak column. A middle fraction was collected and stored over molecular sieves. The material was shown to be pure by g.l.c.

Purification of benzene:

Commercial benzene (Shawinigan) was purified by successive washing with three portions concentrated sulfuric acid, two portions water, and two portions of saturated sodium bicarbonate. The benzene was dried over magnesium sulfate and distilled from sodium metal through a Vigreux column. A middle fraction, shown to be pure by g.l.c., was collected and stored in a tightly stoppered container over molecular sieves.

Purification of bromobenzene:

Commercial bromobenzene (Matheson, Coleman, and Bell) was purified in the same manner as was chlorobenzene. It

was distilled from phosphorus pentoxide through a 4-foot Podbielniak column. A middle fraction, shown to be pure by g.l.c., was collected and stored over molecular sieves.

Methyl ethyl ketazine, 1:

The synthesis of this compound was based on a previously described method (90). Into a 2000 ml 3-necked flask equipped with a magnetic stirrer, reflux condenser, and dropping funnel was added 440 g (6 moles) of methyl ethyl ketone in 400 ml 98% ethanol. A solution of 150 g (3 moles) of 85% hydrazine hydrate in 150 ml ethanol was added (80 minutes) to the stirred solution. The solution was held at reflux for 18 hours. Upon distillation, a greenish-coloured product was collected, 268 g (64%), b.p. 159-163° (704 mm), n_D^{25} 1.4530. Reported (91) b.p. 62-64° (15 mm), n_D^{25} 1.4538.

The n.m.r. spectrum (neat) showed absorption at τ 7.75 quartet (q) ($J=7.5$ cps), τ 8.1 singlet (s), τ 8.2 (s), and τ 8.88 triplet (t) ($J=7.5$ cps), ratio 2.1 : 2.9 : 3.0, required 2 : 3 : 3. The integration of the two singlets was combined.

2-Phenyl-2-butylhydrazine, 4:

In a 5 l 3-necked flask fitted with a mechanical stirrer, reflux condenser and a 2 l dropping funnel, a Grignard reagent was prepared from 56 g (2.3 moles)

magnesium turnings, 340 g (2.16 moles) bromobenzene, and 1950 ml ether. It was stirred and held at reflux for 2 hours. To this solution was added (4 hours) 140 g (1 mole) methyl ethyl ketazine, 1, dissolved in 750 ml ether (90).

After being stirred and held at reflux for 5.5 days, the yellow-coloured solution was poured into 350 ml of an ice-cooled, saturated ammonium chloride solution. The viscous residue which resulted after decantation of the ether, was extracted several times with fresh ether. To the combined ether fractions was added 100 g oxalic acid dihydrate dissolved in 300 ml 98% ethanol. After standing overnight the precipitate was filtered and washed with ether, yielding 129 g of the crude oxalate, 3, m.p. 118-123°. Reported (91) m.p. 131-132° for purified oxalate salt.

The impure hydrazine oxalate salt, 50 g, was slowly added to 400 ml of an aqueous solution of 50 g sodium bicarbonate. Nitrogen was continuously bubbled into the solution. After extracting this solution twice with methylene chloride, the methylene chloride extracts were combined and dried over sodium carbonate. The solution was concentrated on the rotary evaporator and the residue was distilled under a nitrogen atmosphere to yield 20 g (62%) of 4, b.p. 90° (1.4 mm), n_D^{25} 1.5365. Reported (91) b.p. 81-84° (0.4 mm), n_D^{25} 1.5354.

The n.m.r. spectrum (CCl_4) showed absorption at τ 2.72 broad (b), τ 6.93 (s), τ 8.35 (q) ($J=7$ cps), τ 8.65 (s), and τ 9.28 (t) ($J=7$ cps), ratio 4.9 : 3.0 : 2.1 : 3.0 : 3.1, required 5 : 3 : 2 : 3 : 3.

Acetone 2-phenyl-2-butylhydrazone, 5:

To a 3-necked flask equipped with a magnet stirrer, reflux condenser, and dropping funnel was added 7.5 g magnesium sulfate and 133 ml reagent grade acetone. The reaction was done under a blanket of nitrogen. After adding (5 minutes) 20 g of 2-phenyl-2-butylhydrazine, 4, the flask was kept at 40-50° for 2 hours (90). The solution was stirred for 12 hours at room temperature and then concentrated. The residue was distilled to yield 21 g (84%) of 5, b.p. 82° (0.6 mm), n_D^{27} 1.5219. The infrared spectrum (neat) showed a weak absorption at 1685 cm^{-1} (C=N stretching vibration (92)).

The n.m.r. spectrum (CCl_4) showed absorption at τ 2.75 (b), τ 5.5 very broad, τ 8.15 (q) ($J=7.5$ cps), τ 8.17 (s), τ 8.34 (s), τ 8.65 (s), and τ 9.35 (t) ($J=7.5$ cps), ratio 4.95 : 0.70 : 7.85 : 3.10 : 3.00, required 5 : 1 : 8 : 3 : 3. The integration of two overlapping singlets at τ 8.17 and τ 8.34 and of the quartet was combined.

1-Ethyl-1'-methyl-1-phenylazoethane, 7:

Method A; Lithium aluminium hydride reduction:

This reduction procedure was a modification of that

described by Seltzer (34). The hydrazone solution, 2.0 g (0.01 moles) of 5 dissolved in 20 ml ether, was slowly added (3 hours) to a 100 ml stirred ether solution of 0.505 g (0.013 moles) lithium aluminium hydride. The nitrogen blanketed solution was stirred and kept at reflux for 3 days.

Upon cooling, 0.5 ml water, 1.0 ml 10% potassium hydroxide, and 0.5 ml water were successively added dropwise. After filtration, the hydrazine solution was oxidized by stirring for 8 hours in an unstoppered erlenmeyer flask. The ether solution was washed with water to remove the hydrogen peroxide formed, dried over sodium carbonate and concentrated.

The residue was chromatographed in a 30 cm x 1.5 cm column on 30 g of neutral alumina. A green band was eluted at room temperature with the first 50 ml of pentane eluant. Concentration of this solution on the rotary evaporator for 8 hours gave 1.1 g (55%) of 7 as a green oil, n_D^{25} 1.4932. The flask was wrapped with aluminium foil to exclude light during concentration.

The infrared spectrum (CCl_4) showed a weak absorption at 1580 cm^{-1} (N=N stretching) and a doublet at 1380 cm^{-1} and 1370 cm^{-1} (isopropyl group). The ultraviolet spectrum (ether) showed λ_{max} 368 m μ . $\log \epsilon$ 1.46.

The n.m.r. spectrum (CCl_4) showed peaks at τ 2.62 (b), τ 6.25 (m) ($J=6.5$ cps), τ 8.04 (q) ($J=7.5$), τ 8.62 (s), τ 8.75 doublet (d) ($J=6.5$ cps), and τ 9.34 (t) ($J=7.5$ cps), ratio 5.0 : 1.0 : 2.2 : 3.3 : 5.1 : 3.1, required 5 : 1 : 2 : 3 : 6 : 3.

Method B; Diborane Reduction:

Diborane was generated in situ as described previously (93). Boron trifluoride etherate was distilled prior to use, b.p. 47° (15 mm).

To 2.774 g (0.0136 moles) of acetone 2-phenyl-2-butyl-hydrazone, 5, in 75 ml ether in a 3-necked 250 ml flask was added a 40 ml ether solution of 1.2 g (0.0085 moles) boron trifluoride etherate. A viscous, oily material generally formed. After slowly adding (1.5 hours) 0.280 g (0.074 moles) lithium aluminium hydride in 60 ml ether, the contents of the flask were stirred at room temperature for 4 hours. The flask was then cooled in an ice-bath and gaseous hydrogen chloride, generated by dropwise addition of concentrated sulfuric acid onto solid sodium chloride, was conducted into the cooled solution. After stirring for an additional 0.5 hours, 5 g of solid was collected.

This was added to 100 ml of ether in a 3-necked 250 ml flask equipped with a magnetic stirrer and reflux con-

denser. The entire sequence of steps was carried out in an atmosphere of nitrogen. To the stirred slurry at 0° was slowly added a concentrated potassium hydroxide solution. After separation of the two fractions, the ether solution was dried over sodium carbonate. A portion of this solution was concentrated and the residue was transferred to a n.m.r. tube for analysis.

The n.m.r. spectrum (CCl_4) showed peaks at τ 2.85 (b), τ 7.32 (m) ($J = 6$ cps), τ 7.52 (s) which was removed when deuterium oxide was added, τ 8.35 (q) ($J = 7.5$ cps), τ 8.7 (s), τ 9.1 doublet of doublets ($J = 6$ cps), and τ 9.4 (t) ($J = 7.5$ cps), ratio 5.4 : 2.9 : 2.3 : 3.1 : 6.1 : 3.0, required 5 : 3 : 2 : 3 : 6 : 3. The spectrum of this hydrazine, 6, showed several very small peaks centered at τ 6.25 which correspond to the azo methine proton absorption region as well as other extra peaks in the τ 8 to τ 9 region.

The remainder of the hydrazine solution was filtered, oxidized, and chromatographed as described in Method A. The n.m.r. spectrum (CCl_4) was the same as that given for 7 in Method A. The yields for this reduction procedure were variable (0 to 35%).

(+)-1-Ethyl-1'-methyl-1-phenylazoethane, (+)-7:

The procedure followed was similar to that described in

Method A. A solution of 30 g hydrazone, 5, in 120 ml ether was added to 8.28 g of lithium aluminium hydride dissolved in 1500 ml ether. After the reaction was terminated by decomposing the intermediate and the excess reducing agent, the solution was filtered through a Buchner funnel. In the ice-cooled 2000 ml filter flask was a 200 ml ether solution of 45 g dibenzoyl tartaric acid (94), m.p. 89-90°, $[\alpha]_D^{25}$ -115.3° (c 1.03, methanol), reported m.p. 89-91° (94), $[\alpha]_D^{25}$ -112.5° (c 1.1, ethanol) (91).

Eight grams of precipitate formed immediately. The remainder of the solution was placed into the refrigerator and allowed to stand undisturbed for 2 days. Small spherical clusters of crystals adhered to the bottom and sides of the flask. After filtration 20 g of crystals were collected. The two lots of crystals were recrystallized twice from a 2:1 98% ethanol-water mixture., 10 ml of solution per gram of crystals. From the first precipitate formed, 1.3 g of white, slender needle-like crystals were collected. From the second precipitate, 7 g were obtained. Both batches of crystals had m.p. 109-110°, $[\alpha]_D^{25}$ -65.2° (c 1, chloroform). Upon cooling the mother liquors, no further precipitate was formed.

Analysis calculated for $C_{31}H_{36}N_2O_8$: C, 65.94; H, 6.43; N, 4.96. Found: C, 65.65; H, 6.23; N, 5.08.

Three grams of the twice recrystallized dibenzoyl tartrate salt was dissolved in 20 ml of 10% potassium hydroxide and the solution was extracted with two 20 ml portions of ether. Several pellets of potassium hydroxide were then added to the aqueous solution which was again extracted with two portions of 20 ml ether. The combined ether extracts were washed with water, dried, and the hydrazine was oxidized to (+)-7 which was isolated as described in Method A. Approximately 0.65 g (65%) of (+)-7 was isolated, n_D^{25} 1.4934, α_D^{25} +35.5° (1 dm., neat).

Analysis calculated for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.12; H, 9.86; N, 13.86.

Optical rotatory dispersion (c 0.0025, cyclohexane):

$[\phi]_{700} + 98^\circ$; $[\phi]_{589} + 130^\circ$; $[\phi]_{500} + 230^\circ$; $[\phi]_{450} + 408^\circ$;
 $[\phi]_{410} + 980^\circ$; $[\phi]_{398} + 1110^\circ$; $[\phi]_{380} + 506^\circ$; $[\phi]_{374} 0^\circ$;
 $[\phi]_{360} - 945^\circ$; $[\phi]_{346} - 127^\circ$; $[\phi]_{310} - 620^\circ$.

The curve is given in Figure 1.

The molecular rotations, $[\phi]$, were calculated from the formulae (74)

$$[\alpha] = \frac{\alpha}{c \cdot l}$$

$$[\phi] = \frac{[\alpha]M}{100}$$

where

α = observed rotation on the chart

$[\alpha]$ = specific rotation

c = concentration in g/ml

l = length of cell in dm

M = molecular weight of the compound

The magnitude of the molecular rotations and the wavelength of the peak and trough compare favourably with those reported by Kosower (114) for optically active 1-ethyl-1-phenyl-bis-azoethane.

2-Phenylbutanoic nitrile, 9:

2-Phenylbutyramide (173 g) was dehydrated as previously described (95) to give 130 g (85%) of 9, b.p. 117-119° (14 mm), n_D^{24} 1.5080. Reported (95) b.p. 122-124° (16 mm), n_D^{25} 1.5070 and (96) n_D^{25} 1.5075. The infrared spectrum (neat) showed a sharp absorption at 2250 cm^{-1} (nitrile).

The n.m.r. spectrum (CCl_4) showed absorption at τ 2.7 (s), τ 6.35 (t) ($J=7$ cps), τ 8.15 (m) ($J=7$ cps), τ 8.95 (t) ($J=7$ cps), ratio 4.85 : 1.0 : 1.93 : 3.0, required 5 : 1 : 2 : 3.

2-Methyl-2-phenylbutanoic nitrile, 10:

The alkylation of 2-phenylbutanoic nitrile was performed by modifying a previously described procedure (97) for methylation of ethers. The nitrile, 10 g (0.069 moles),

methyl iodide, 11.3 g (0.079 moles), and 40 ml of dimethoxyethane distilled previously from lithium aluminium hydride were added to a 3-necked 250 ml flask equipped with a magnetic stirrer, reflux condenser, and an easily removeable stopper. Sodium hydride, 1.9 g (0.079 moles), was washed with dimethoxyethane, filtered, and protected from the air. Small portions of sodium hydride were added to the ice-cooled flask. It was necessary to warm the flask slightly to initiate the reaction. During 2 hours small portions of sodium hydride were added after hydrogen gas evolution subsided. A further 4 g of methyl iodide was added and the mixture was stirred at room temperature for 10 hours.

Ethanol was added to the maroon-coloured solution to decompose unreacted sodium hydride. After concentration of the solution on the rotary evaporator, water and ether were added. The ether extract was successively washed with solutions of sodium bisulfite, sodium bicarbonate and water, dried over sodium sulfate, and concentrated.

From the n.m.r. spectrum an estimated 5% unalkylated nitrile was present. The latter was preferentially saponified (95) by maintaining the solution of the products in 20 ml 98% ethanol and 0.6 g potassium hydroxide at reflux. The crude product was distilled to yield 9.8 g (84%) of 10, b.p. 56° (0.25 mm), n_D^{25} 1.5033. Reported

(95) n_D^{25} 1.5036. Only one peak appeared when analyzed by g.l.c. The infrared spectrum (neat) showed an absorption at 2250 cm^{-1} (nitrile).

The n.m.r. spectrum (CCl_4) showed peaks at $\tau 2.65$ (b), $\tau 8.1$ (q) ($J=7$ cps), $\tau 8.34$ (s), and $\tau 9.06$ (t) ($J=7$ cps), ratio 5.0 : 2.0 : 2.9 : 3.0, required 5 : 2 : 3 : 3.

2-Methyl-2-phenylbutanoic acid, 11:

2-Methyl-2-phenylbutanoic nitrile, 209 g (1.31 moles), was saponified by 124 g (2.22 moles) potassium hydroxide dissolved in 1000 ml diethylene glycol as described previously (95). Distillation yielded a yellow oil, 195 g (83.5%), b.p. $120-122^\circ$ (0.9 mm). The oil which readily solidified was crystallized from 200 ml pentane to yield 169 g (73%) of 11, m.p. $55-56^\circ$. Reported (98) m.p. $56-57^\circ$.

(-)-2-Methyl-2-phenylbutanoic acid, (-)-11:

2-Methyl-2-phenylbutanoic acid, 157 g (0.88 moles), was resolved as the quinine salt (98) using 204 g (0.63 moles) quinine. After 3 recrystallizations of the salt, the recovered acid had $[\alpha]_D^{25} -21.2^\circ$ (c 4.8, benzene). After 4 recrystallizations of the salt, 22 g of the recovered acid was isolated, m.p. $87-87.5^\circ$, $[\alpha]_D^{25} -29.06^\circ$ (c 4.8, benzene). Reported (98) m.p. $86-87^\circ$, $[\alpha]_D^{25} -30.0^\circ$ (c 4.8, benzene).

2-Methyl-2-phenylbutyryl chloride, 12:

2-Methyl-2-phenylbutanoic acid, 12.6 g (0.07 moles), and 17 g (0.14 moles) thionyl chloride were mixed and allowed to stand at room temperature for 16 hours. The subsequent workup was done as previously described (98). Distillation yielded 13 g (93%) of 12, b.p. 59-62° (0.15 mm), n_D^{27} 1.5196. Reported (98) b.p. 122-124° (16 mm).

The n.m.r. spectrum (CCl_4) showed peaks at τ 2.75 (s), τ 7.9 two superimposed quartets ($J=7.5$ cps), τ 8.29 (s), and τ 9.0 (t) ($J=7.5$ cps), ratio 4.8 : 2.0 : 3.0 : 3.0, required 5 : 2 : 3 : 3.

Similarly from 11.5 g of (-)-2-methyl-2-phenylbutanoic acid, $[\alpha]_D^{25}$ -29.06° (c 4.8, benzene), there was obtained 11 g (87%) of the acid chloride, b.p. 57° (0.05 mm), n_D^{28} 1.5193.

2,3-Dimethyl-3-phenyl-2-pentanol, 13:

To a two-fold excess of well stirred methyllithium prepared from 3.7 g (0.528 moles) lithium metal, 37.5 g (0.264 moles) methyl iodide, and 200 ml ether (99) and held at -60° was added 13 g (0.066 moles) of 2-methyl-2-phenylbutyryl chloride in 90 ml ether. The acid chloride was quickly added. The solution was warmed to 0°.

To the ice-cooled solution was added a 100 ml solution of 30 g ammonium chloride. The aqueous portion was extracted with ether. All the ether solutions were combined and successively washed with solutions of sodium bisulfite, sodium bicarbonate, and water, then dried over magnesium sulfate. A small portion of the ether solution was concentrated. The infrared spectrum (CCl_4) of the concentrate showed absorption at 3560 cm^{-1} (OH stretching) and at 1710 cm^{-1} (carbonyl stretching).

The alcohol-ketone solution was reacted again with excess methyllithium as described above. Upon work-up and drying, the ether was distilled through a short Vigreux column to yield a 12 g residue. The infrared spectrum (CCl_4) of the residue showed an absorption at 3560 cm^{-1} (OH stretching) and no absorption at 1710 cm^{-1} . The alcohol was not further purified.

In a similar manner the acid chloride, 11 g (0.056 moles), from (-)-2-methyl-2-phenylbutanoic acid was reacted twice with excess methyllithium. After concentration 9.5 g of crude alcohol resulted. The infrared spectrum (neat) showed an absorption at 3450 cm^{-1} (OH stretching) and the absence of a carbonyl absorption.

2-Acetoxy-2,3-dimethyl-3-phenylpentane, 14:

The alcohol, 13, 12 g (0.063 moles), was acetylated

by 10 g (0.128 moles) of acetyl chloride in 30 ml N,N-dimethylaniline according to the acetylation method described by Hammond (100). Distillation of the crude product resulted in 8.5 g (58%) of the acetate, b.p. 88-89° (0.4 mm), n_D^{25} 1.5034.

The n.m.r. spectrum (CCl_4) showed peaks at τ 2.8 (b), τ 7.75 (m) ($J=7.5$ cps), τ 8.14 (s), τ 8.55 (s), τ 8.66 (s), and τ 9.33 (t) ($J=7.5$ cps), ratio 5.13 : 14.2 : 3.0, required 5 : 14 : 3. The integration of the aliphatic protons with the exception of the methyl triplet was combined.

Analysis calculated for $\text{C}_{15}\text{H}_{22}\text{O}_2$: C, 76.88; H, 9.46.
Found: C, 77.06; H, 9.17.

In a similar manner 9.5 g (0.05 moles) of 2,3-dimethyl-3-phenyl-2-pentanol obtained from (-)-2-methyl-2-phenylbutanoic acid was acetylated. Distillation yielded 8 g (69%) of product, b.p. 81° (0.2 mm), n_D^{31} 1.4998. The infrared spectrum (neat) showed a strong absorption at 1720 cm^{-1} (carbonyl stretching) and the absence of an OH stretching absorption at 3450 cm^{-1} .

2,3-Dimethyl-3-phenyl-1-pentene, 15:

Method A; Phosphorus oxychloride dehydration:

To 0.5 g of 2,3-dimethyl-3-phenyl-2-pentanol, 13, in 20 ml pyridine was added 0.2 g phosphorus oxychloride. The

contents of the 100 ml round bottom flask were heated to gentle reflux for 1.5 hours. After cooling aqueous hydrochloric acid and ether were added. The ether solution was dried over magnesium sulfate, concentrated, and the residue chromatographed on 30 g neutral alumina. The olefin was eluted with the second 25 ml fraction of Skelly B. The infrared spectrum (CCl_4) showed absorptions at 1635 cm^{-1} and 895 cm^{-1} (terminal olefin).

The n.m.r. spectrum (CCl_4) showed peaks at $\tau 2.83$ (s), $\tau 5.07$ (s), $\tau 8.14$ (q) ($J=7$ cps), $\tau 8.54$ (s), $\tau 8.64$ (s), and $\tau 9.23$ (t) ($J=7$ cps), ratio $5.18 : 1.87 : 2.07 : 6.31 : 3.0$, required $5 : 2 : 2 : 6 : 3$. The integration of the two singlets at $\tau 8.54$ and $\tau 8.64$ was combined.

Method B; Acetate pyrolysis:

The pyrolysis column and the general method followed has been previously described (101). Essentially the column consisted of a pyrex glass tube heated by nichrome wire wound around the tube. The column was filled with clean glass helices up to a height of 12 inches from the bottom. The ester to be pyrolyzed was dissolved in methanol and the solution was dropped through the heated helices. The temperature of pyrolysis was not determined. The optimum condition was determined by pyrolyzing small quantities of ester, 14, and analyzing the product obtained by g.l.c.

for olefin and starting acetate.

To the methanolic solution of pyrolyzed acetate was added an equal volume of water. The solution was washed twice with ether. The ethereal extracts were combined, washed with saturated sodium bicarbonate solution, dried, and concentrated through a short Vigreux column. The residue was distilled through a microdistillation apparatus to yield 0.9 g (61%) of the olefin, 15, b.p. 107-110° (23 mm), n_D^{25} 1.5103. The infrared spectrum (CCl_4) showed absorptions at 1635 cm^{-1} and 895 cm^{-1} (terminal olefin).

The n.m.r. spectrum (CCl_4) showed peaks at $\tau 2.8$ (s), $\tau 5.05$ (s), $\tau 8.12$ (q) ($J=7$ cps), $\tau 8.52$ (s), $\tau 8.66$ (s), and $\tau 9.21$ (t) ($J=7$ cps), ratio 5.1 : 1.9 : 2.1 : 6.2 : 3.0, required 5 : 2 : 2 : 6 : 3. The integration of two singlets at $\tau 8.52$ and $\tau 8.66$ was combined.

Analysis calculated for $\text{C}_{13}\text{H}_{18}$: C, 89.58; H, 10.41.
Found: C, 89.80; H, 10.60.

(+)-2,3-Dimethyl-3-phenyl-1-pentene, (+)-15:

2-Acetoxy-2,3-dimethyl-3-phenylpentane (8 g) obtained from the sequence of steps beginning from (-)-2-methyl-2-phenylbutanoic acid was pyrolyzed as described above to yield 4.5 g of undistilled olefin. A portion of this residue was distilled through the microdistillation apparatus,

b.p. 105-109° (21 mm), n_D^{29} 1.5101, α_D^{25} +11.3° (1 l dm., neat). Analysis by g.l.c. showed this olefin to be at least 97% pure.

2,3-Dimethyl-3-phenylpentane, 16:

2,3-Dimethyl-3-phenyl-1-pentene (1 g) in 20 ml 98% ethanol was hydrogenated over 100 mg 5% rhodium on alumina at room temperature and atmospheric pressure. The theoretical amount of hydrogen was taken up in the first hour, but hydrogenation was continued for 24 hours. After the catalyst was filtered, the solvent was concentrated by distilling through the microdistillation apparatus to yield 16, b.p. 105-107° (21 mm), n_D^{27} 1.5012. From g.l.c. analysis the hydrocarbon was estimated to be at least 97% pure and free of olefin. The infrared spectrum (CCl_4) showed the absence of absorption at 1635 cm^{-1} and 895 cm^{-1} .

The n.m.r. spectrum (CCl_4) showed peaks at τ 2.86 (s), τ 7.9 to τ 8.7 complex multiplet, τ 8.83 (s), τ 9.1 (d) and τ 9.35 (d) ($J=6.5$ cps), and τ 9.31 (t) ($J=7$ cps), ratio 5.0 : 15.9, required 5 : 15. The integration of the aliphatic protons was combined.

Analysis calculated for $\text{C}_{13}\text{H}_{20}$: C, 88.57; H, 11.43.
Found: C, 88.89; H, 11.48.

(-)-2,3-Dimethyl-3-phenyl-1-pentene, (-)-16:

(+)-2,3-Dimethyl-3-phenyl-1-pentene, α_D^{25} +11.3° (1

1 dm., neat) was hydrogenated exactly as described above. Distillation through the microdistillation apparatus yielded the saturated hydrocarbon, (-)-16, b.p. 108-111° (23 mm), n_D^{26} 1.5012, α_D^{25} -0.4° (1 dm., neat). Analysis by g.l.c. indicated that the hydrocarbon was greater than 98% pure and free of olefin.

Optical rotatory dispersion (0.0105, methanol):

$[\phi]_{350}$ - 13°; $[\phi]_{325}$ - 34°; $[\phi]_{310}$ - 58°; $[\phi]_{300}$ - 42°;
 $[\phi]_{293}$ 0°; $[\phi]_{290}$ + 15°; $[\phi]_{280}$ + 89°.

The curve is shown in Figure 2.

2-Phenyl-1-butanol, 18:

2-Phenylbutanoic acid, 17, (16.4 g or 0.1 moles), was reduced with 4.75 g (0.125 moles) lithium aluminium hydride as previously described (102). Upon distillation 12.5 g (83%) of 18, b.p. 83° (2 mm) was isolated. Reported (115) b.p. 81° (2 mm).

The n.m.r. spectrum ($CDCl_3$) showed peaks at τ 2.85 (s), τ 6.5 (d) ($J=6.5$ cps), τ 7.5 (m), τ 8.4 (m), and τ 9.24 (t) ($J=7$ cps), ratio 4.9 : 1.9 : 1.0 : 1.1 : 2.0 : 3.0, required 5 : 2 : 1 : 1 : 2 : 3.

2-Phenyl-1-butene, 20:

2-Phenyl-1-butanol, 18, 12.5 g (0.083 moles), was acetylated according to the procedure previously described (100). Distillation of the crude product yielded 12.5 g

(78%) of the acetate, 19, b.p. 84-84° (1.6 mm), n_D^{26} 1.4915. Reported (103) b.p. 91° (2 mm), n_D^{25} 1.4915. This acetate was pyrolyzed in the manner described (101). The pyrolysis temperature was about 400°. It was necessary to pass the methanolic solution through the column 4 times to pyrolyze all the ester. The disappearance of the acetate was monitored by g.l.c. After work-up of the reaction mixture, it was distilled through a Nester/Faust Annular Teflon Spinning Band Distillation Column to yield 3 g (35%) of the olefin, 20, b.p. 80° (89 mm), n_D^{25} 1.5271. Reported (103) b.p. 181° (760 mm), n_D^{25} 1.5264.

The n.m.r. spectrum (CCl_4) showed peaks at τ 2.76 (m), τ 4.8 (s), τ 5.0 (s), τ 7.5 (q) ($J=7.5$ cps), and τ 8.94 (t) ($J=7.5$ cps), ratio 5.1 : 1.0 : 1.0 : 2.0 : 3.0, required 5 : 1 : 1 : 2 : 3.

cis-2-Phenyl-2-butene, 22:

The olefin was prepared by the sulfuric acid catalyzed dehydration of 2-phenyl-2-butanol, 21, as described by Cram (104). Gas-liquid chromatography indicated the presence of three compounds in the mixture. Fractional distillation of the three components was not satisfactory. The mixture was concentrated on the spinning band column. The pot residue was distilled through the microdistillation apparatus to yield the cis olefin, b.p. 86° (20 mm), n_D^{27} 1.5388. Re-

ported (104) b.p. 94° (29.6 mm), n_D^{25} 1.5393. Analysis by g.l.c. indicated purity of approximately 97%.

The n.m.r. spectrum (CCl_4) showed peaks at τ 2.78 (b), τ 4.13 split quartet ($J=6.5$ cps), τ 8.0 (s), and τ 8.2 doublet of doublets ($J=6.5$ cps), ratio 5.22 : 1.00 : 3.05 : 3.00, required 5 : 1 : 3 : 3.

The forerun from the above concentration was fractionated. The lower boiling component had the same retention time on g.l.c. and the same n.m.r. spectrum as did 2-phenyl-1-butene, 20. The other component of the mixture was assumed to be trans-2-phenyl-2-butene, 23.

3,4-Dimethyl-3,4-diphenylhexane, 24, 25:

2-Phenylbutane, 24 g (0.18 moles) and di-tert.-butyl peroxide, 17 g (0.12 moles), were heated together for 72 hours as described previously (105). After removal of all volatile fractions by using the water aspirator, distillation yielded an oil, b.p. 126° (0.1 mm). The oil was dissolved in methanol and cooled to yield a precipitate which after 5 recrystallizations gave the meso dimer, 24, m.p. $94-95^{\circ}$. Reported (105) m.p. 93° .

The n.m.r. spectrum (CCl_3) showed peaks at τ 2.95 (b), τ 7.82 (m) ($J=7$ cps), τ 8.50 (m) ($J=7$ cps), τ 8.7 (s), and τ 9.45 (t) ($J=7$ cps), ratio 5.0 : 4.9 : 3.1, required

5 : 5 : 3. The integration of the two multiplets and the singlet was combined.

The residue and the mother liquors from the recrystallizations of the meso dimer were combined and concentrated. The concentrate was distilled, b.p. 113° (0.05 mm). Reported (105) b.p. 135-138° (0.5 mm). The distillate was placed in the refrigerator and after a week 0.65 g of the dl dimer, 25, m.p. 39-41° formed. Reported (105) m.p. 40-41°.

The n.m.r. spectrum (CCl_4) showed peaks at τ 2.98 (b), τ 7.5 to τ 8.6 (m), τ 8.75 (s), and τ 9.41 (t) ($J=7$ cps), ratio 5.0 : 5.2 : 2.8, required 5 : 5 : 3. The integration of the multiplets and the singlet was combined.

1-(2-Butyl)-4-(2-propyl)-benzene, 26:

2-Phenylbutane, 5 g, and 2 g of 2-propyl chloride were added to a 125 ml ice-cooled suction flask connected to the water aspirator. One gram of aluminium chloride was added in 4 portions to the suction flask. After standing for 1 hour in the ice bath, the reaction mixture was washed with water, dried, and analyzed by g.l.c. A mixture of starting material and 9 other compounds were present. The major product peak was collected from the effluent of the gas chromatograph. After collecting approximately 100 mg, the material was further purified

by reinjecting and trapping the major component n_D^{25} 1.4879. Reported (106) n_D^{20} 1.4876 and (107) n_D^{20} 1.4910. The purity of the hydrocarbon was estimated to be at least 98%. The infrared spectrum (CCl_4) showed a sharp absorption of medium intensity at 825 cm^{-1} (para di-substituted benzene).

The n.m.r. spectrum (CCl_4) showed peaks at τ 2.95 (s), τ 7.32 (m) ($J=7$ cps), τ 8.43 (q) ($J=7$ cps), τ 8.75 two superimposed doublets ($J=7$ cps), and τ 9.18 (t) ($J=7$ cps), ratio 4.1 : 16.0, required 4 : 16. The integration of all the aliphatic protons was combined.

2-Phenyl-2-butylamine, 27:

Method A; Schmidt Reaction:

(-)-2-Methyl-2-phenylbutanoic acid, (-)-11, $[\alpha]_D^{25}$ -29.06° (c 4.8, benzene), (1 g) was added to 2 ml of concentrated sulfuric acid and 8 ml of chloroform as described (108) for hydratropic acid. To the stirred solution maintained at 45°, was slowly added 440 mg of sodium azide. After work-up (108) and concentration, the major component of the mixture was collected from the effluent of the gas chromatogram. The infrared spectrum (CCl_4) showed a doublet at 3500 cm^{-1} and 3400 cm^{-1} (primary amine) and the absence of aliphatic C-H stretching vibrations in the 3000 cm^{-1} to 2900 cm^{-1} region.

The n.m.r. spectrum (CCl_4) showed peaks at $\tau 2.8$ to $\tau 3.7$ (m) and $\tau 6.6$ broad singlet, ratio 5 : 2. It would appear that aniline and not 2-phenyl-2-butylamine was recovered.

Method B; Curtius rearrangement:

2-Methyl-2-phenylbutyryl chloride, 3 g, obtained from (+)-2-methyl-2-phenylbutanoic acid, $[\alpha]_D^{25}$ 6.60° (c 4.8, benzene), 1 g of activated sodium azide (109), and 10 ml of 1,2-dimethylbenzene were allowed to react as previously described (91). The ether extract was concentrated by distillation through a short Vigreux column. The amine was collected from the effluent of the gas chromatograph, n_D^{25} 1.5164, α_D^{25} -3.42° (1 1 dm., neat). Reported (91) n_D^{25} 1.5148. The amine had an estimated purity of at least 98%. The infrared spectrum (CCl_4) showed absorptions at 3495 cm^{-1} and 3405 cm^{-1} (primary amine) and C-H stretching at 2990 cm^{-1} .

The n.m.r. spectrum (CCl_4) showed peaks at $\tau 2.8$ (b), $\tau 8.3$ (q) ($J=7$ cps), $\tau 8.64$ (s) which disappeared upon exchange with deuterium oxide, and $\tau 9.28$ (t) ($J=7$ cps), ratio 5.0 : 2.1 : 4.9 : 3.1, required 5 : 2 : 5 : 3. The integration of the two singlets in the unexchanged spectrum was combined.

Attempted isomerization of 7:

Method A; Anhydrous hydrogen chloride:

Twenty ml of ether in a 100 ml erlenmeyer flask were saturated with gaseous hydrogen chloride generated by slowly dropping concentrated sulfuric acid onto sodium chloride. The ether solution was cooled to 0° and 0.5 g of 1-ethyl-1'-methyl-1-phenylazoethane, 7, was added. The mixture, kept in an ice bath, was stirred for about six hours and concentrated. The residue was analyzed by n.m.r. and found to have the same spectrum as did 7.

Method B: Potassium tert-butoxide:

To 0.3 g (0.00147 moles) of 7 in 30 ml of dry dimethyl sulfoxide was added 0.165 g (0.00147 moles) potassium tert-butoxide prepared as described (112). The colour of the solution changed from a light yellow to dark brown upon standing at room temperature overnight. To this solution was added water and ether. The ether extract was washed several times with water, dried over sodium carbonate, concentrated and analyzed by n.m.r. The n.m.r. spectrum was complex and qualitatively indicated the presence of hydrazone, 5, starting azo compound, 7, and other peaks not accounted for. The addition of an alcoholic solution of oxalic acid dihydrate to an ether solution of the mixture did not result in formation of any precipitate.

Hydrogenolysis of (+)-7:

To 1.0 g of (+)-7, $\alpha_D^{25} +35.5^\circ$ (1 l dm., neat), in 100 ml of methanol in a 200 ml round-bottom flask was added about 4.5 g Raney nickel (113). The solution was hydrogenated at room temperature and atmospheric pressure. Approximately one equivalent of hydrogen, 114 ml, was taken up in 4 hours. No further hydrogen was consumed. The contents of the flask were then held at reflux for 11 hours.

The catalyst was filtered and the methanol was distilled through a Vigreux column. The residue was dissolved in ether. The solution was washed with aqueous hydrochloric acid and the acidic solution was neutralized by adding a concentrated solution of potassium hydroxide. The insoluble material was dissolved in ether. The ether solution was dried over potassium carbonate, and concentrated by distillation through a short Vigreux column. The amine was collected from the effluent of the gas chromatograph. Approximately 200 mg of an estimated 98% pure 27, $n_D^{25} 1.5146$, $\alpha_D^{25} -14.0^\circ$ (1 l dm., neat) was collected. Reported (91) $n_D^{25} 1.5148$, $\alpha_{546}^{25} -18.2^\circ$ (1 l dm., neat), $\alpha_D^{25} +16.8^\circ$ (1 l dm., neat) (114). The n.m.r. spectrum (CCl_4) showed peaks at $\tau 2.75$ (b) $\tau 8.32$ (q) ($J=7.5$ cps), $\tau 8.65$ (s), $\tau 8.85$ (s) which disappeared upon shaking with deuterium oxide, and $\tau 9.35$ (t) ($J=7.5$ cps),

ratio 4.97 : 2.05 : 3.08 : 2.05 : 3.0, required 5 : 2 :
3 : 2 : 3.

Rate of decomposition of 7:

Method: The kinetics were followed by measuring the rate of nitrogen evolution.

Solvent: Reagent grade cumene was washed consecutively with 3 portions of concentrated sulfuric acid, water, and with two portions of saturated sodium bicarbonate. After drying over magnesium sulfate, the solvent was distilled through a 4-foot Podbielniak column. A middle fraction was collected and stored over molecular sieves.

Apparatus: The apparatus used has been previously described (110). Essentially it consisted of a 10 ml reaction flask with a standard tapered joint. The open end of the flask was covered by a rubber serum cap. A small diameter side-arm was connected via a fine capillary to a thermostatted gas-burette. The reaction flask was immersed into a 3-necked flask in which a solvent was held at reflux.

Procedure: The general procedure followed has been previously described (110). The azo compound (0.102 g) was dissolved in 2 ml cumene and the solution was placed into the reaction flask. After flushing the flask well with nitrogen and connecting to the jacketed gas-burette, the

reaction flask was immersed into the refluxing heating solvent. The volume of nitrogen evolved was measured at regular intervals of time. Readings were taken for a period of 12 hours. The volume of nitrogen at infinite time was measured after about 9 half-lives. From the plot of $(V_{\infty} - V_t)$ versus time, the rate constant for the azo compound decomposition was calculated. A sample calculation is given in Table I.

The vapour of the boiling liquid served as the heating bath. The temperature of the vapour of the boiling liquid, 122.5° n-octane, was recorded and taken as the temperature of decomposition. A typical plot of $(V_{\infty} - V_t)$ versus time is shown in Figure 3. The results are given in Table II.

Product analysis:

The azo compound was decomposed in an evacuated sealed-tube. Cylindrical glass tubing of 5 mm diameter was used in all experiments. Glass tubing was used to construct the figure "H". The two lower ends were sealed. To the middle of the horizontal tube was attached a short piece of tubing parallel to the two vertical ends. The entire assembly was filled with concentrated sulfuric acid and permitted to stand for a minimum of 4 hours. The acid was poured out and the assembly was rinsed with water and then filled with con-

centrated ammonium hydroxide. After standing overnight, the ammonia solution was drained and the glass frame was baked for 3 hours in an oven heated to 130°.

The assembly was attached to the glass connection of the high vacuum rack. The solutions of the azo compound to be decomposed were added to the two vertical, open-ended tubes which were afterwards sealed. The tubes were degassed at a pressure of approximately 10^{-4} mm by a succession of freeze-thaw cycles. After removal of the dissolved gases, the tubes were sealed just below the horizontal bar of the "H". Overall length of the sealed tubes was about 10 cm.

Generally about 35 mg of the azo compound was dissolved in 350 mg of benzene or 1 M butanethiol in benzene. The sealed tubes were individually wrapped in aluminium foil and placed into preheated ovens maintained at $100 \pm 1^\circ$ or $125 \pm 1^\circ$. The tubes placed in the oven set at 125° were removed after 14 hours (10 half-lives). Those placed in the oven set at 100° were removed after 130 hours (at least 10 half-lives).

Product analysis of unscavenged decomposition:

After the azo compound had completely decomposed, the sealed tubes were opened and analyzed. The solution was chromatographed on about 5 g of neutral alumina.

Fifteen ml of pentane was used as eluant. If a larger volume were used, hydrazone would be eluted from the column. The pentane eluant was concentrated by distillation through a short Vigreux column. The flask containing the residue was stoppered with a rubber serum cap and weighed. Through the serum cap was injected bromobenzene which was used as the internal standard. The amount of bromobenzene added was taken as the difference in the weights.

The flask contents were analyzed on the Aerograph 202 fractometer. The peak areas were computed by multiplying the peak height by the peak width at one-half height. Response factors of authentic decomposition products were determined and used in estimating the products resulting from the decomposition of the azo compound. Duplicate samples were done at each temperature. Four determinations were made on each sample. A summary of the results is presented in Table IV.

The response factors for the unscavenged decompositions were calculated as follows:

$$\frac{\text{moles of B}}{\text{moles of A}} = \frac{\text{area of B}}{\text{area of A}} \times \frac{\text{response of B}}{\text{response of A}}$$

if response of A = 100

$$\text{then response of B} = \frac{\text{moles of B}}{\text{moles of A}} \times \frac{\text{area of A}}{\text{area of B}} \times 100$$

On this basis the response factors for bromobenzene: 2-phenylbutane : 2-phenyl-1-butene: cis-2-phenyl-2-butene : 2,3-dimethyl-3-phenylpentane : 3,4-dimethyl-3,4-diphenylhexane were 100 : 83.8 : 85.4 : 85.4 : 74.4: 173.0.

For the scavenged determinations the response factors for bromobenzene : 2-phenylbutane : 2,3-dimethyl-3-phenylpentane were 100 : 79.3 : 67.6. No symmetrical dimer, 3,4-dimethyl-3,4-diphenylhexane, was observed. Olefins were present in such minute quantities that they were not analyzed.

In a typical analysis the injector temperature was set at 235° and the detector at 245°. The initial temperature of the column was 75°. The instrument was programmed so that the column temperature increased 3° per minute with a gas flow of 50 ml per minute. At a column temperature of 160° the gas flow was boosted to 150 ml per minute until the last component was eluted.

Product analysis of butanethiol scavenged decomposition:

The sealed tubes were prepared for analysis as described previously for the unscavenged runs.

The analysis was performed under similar conditions. The temperature programme was begun at 90° column temperature. The rate of column temperature increase was 1.5° per minute with a gas flow rate of 90 ml per minute. The results are summarized in Table V.

Decomposition of (+)-7:

The azo compound, (+)-7, $\alpha_D^{25} +35.5^\circ$ (1 l dm., neat), (1.8 g), was dissolved in about 20 ml of 1 M butanethiol in benzene. The solution was poured into a 75 ml capacity Hooke stainless steel pressure bomb which had been previously treated with concentrated ammonium hydroxide solution and baked for 5 hours at 130° . The solution was well flushed with nitrogen and stoppered. The bomb was placed into a preheated oven maintained at $100 \pm 1^\circ$ or $125 \pm 1^\circ$.

Three scavenged decompositions of (+)-7 were done. Two determinations were at 125° decomposition; 1.812 g (+)-7 in 1.671 g butanethiol and 15 ml chlorobenzene and 1.814 g (+)-7 in 20 ml of 1 M butanethiol in benzene. A third decomposition was done at 100° on 1.842 g (+)-7 in 20 ml of 1 M butanethiol in benzene.

Separation and isolation of 2-phenylbutane and 16:

After the bomb was taken out of the oven, it was cooled and opened. The contents were concentrated by slow distillation through a short Vigreux column. To this concentrate was added 10 ml of glacial acetic acid and 2 ml of trichlorosulphenyl chloride (lll). After heating on the steam bath for 1 hour, the mixture was cooled and 100 ml pentane added. The pentane was extracted 7 times with

water and dried over magnesium sulfate. The pentane solution was concentrated by distillation through a short Vigreux column. The residue was chromatographed on about 200 g of activated basic alumina. Through the jacket of the 1 m x 2 cm column was circulated ice-water. Pentane, 25 ml fractions, was used as the eluting solvent. Each fraction was analyzed by g.l.c. for eluted hydrocarbons which were generally eluted between the fifth and seventh fraction.

2-Phenylbutane and 2,3-dimethyl-3-phenylpentane, 16, were isolated from the effluent of the gas chromatograph. Isothermal conditions, 150° column temperature, and a gas flow of 150 ml per minute were used. The rotation of 2-phenylbutane was taken on the Rudolph Polarimeter. Samples of 16 were submitted for o.r.d. determination. The results are summarized in Table VI. Figures 4 and 5 show the curves obtained. Infrared spectra of the hydrocarbons corresponded to those of authentic compounds.

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